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# PAPER

# Synthesis, characterization and photophysical properties of $PPh_2-C_2-(C_6H_4)_n-C_2-PPh_2$ based bimetallic Au(I) complexes<sup>†</sup>

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A family of the diphosphines PPh<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>C<sub>2</sub>PPh<sub>2</sub> (n = 0-3), which possess a dialkynyl-arene spacer between the phosphorus atoms, was used for the synthesis of a series of bimetallic gold(1) complexes 1–7. Unlike the corresponding polynuclear Au(1) clusters, which show unique phosphorescence, 1–7 reveal dual emissions consisting of fluorescence and phosphorescence. The results are rationalized, in a semiquantitative manner, by the trace (1–3) to zero (4–7) contribution of MLCT varying with the number of conjugated phenylene rings. As a result, unlike typical polynuclear Au(1) clusters with 100% triplet state population, the rate constant of the  $S_1 \rightarrow T_1$  intersystem crossing is drastically reduced to  $10^9 \text{ s}^{-1}$  (4–7)– $10^{10} \text{ s}^{-1}$  (1–3), so that the fluorescence radiative decay rate can compete or even dominates. The drastic  $O_2$ quenching of phosphorescence demonstrates the unprotected nature of the emission chromophores in 1– 7, as opposed to the well protected,  $O_2$  independent phosphorescence in most multimetallic Au(1) clusters.

# Introduction

The photophysical properties of gold complexes are of fundamental importance and have been actively studied for several decades.<sup>1-5</sup> Relevant research has been stimulating significant progress in preparative gold chemistry as well as attracting considerable theoretical attention.<sup>6</sup> Among numerous gold-containing species, the phosphine-alkynyl complexes are of particular interest due to their ease of preparation and handling, wide range of accessible modifications of the constituent ligands, fascinating structural assemblies and intriguing photoluminescent characteristics.<sup>3,7-10</sup> Much of the research effort has been devoted to the systematic investigation of the emission originating from gold-perturbed intraligand alkynyl transitions.<sup>5,8,11,12</sup> As has been shown, binding of Au(I) ions to -C=CR moieties may induce the triplet state emission of the organic ligand due to fast intersystem crossing promoted by spin-orbit coupling of the heavy gold atom. Surprisingly, the metal-modified emission of the phosphines has been much less studied, though these ligands possessing conjugated backbones proved to be useful building blocks in the construction of both molecular entities and polymeric materials and demonstrated promising light emissive properties.13 The examples available in the literature clearly indicate that coordination of the gold(I) centers to the phosphorus-containing chromophores results in a large increase in the emission quantum efficiency<sup>14</sup> as the presence of the d<sup>10</sup> ion diminishes the ability of the polarizable phosphorus lone pair to participate in nonradiative decay processes (*e.g.*, photoinduced-electron-transfer quenching).<sup>15</sup> Additionally, it has been demonstrated that the effect of the heavy Au(I) ion bound to a phosphine with a polyaromatic substituent such as phenanthrene leads to the appearance of pertinent room-temperature phosphorescence originating from an aromatic ligand, *i.e.*, the phenanthrene moiety.<sup>16</sup>

Recently, we have been extensively using bidentate phosphine ligands with polyaromatic backbones in the synthesis of polynuclear luminescent gold(1)-containing alkynyl compounds.<sup>17-20</sup> The resulting complexes exhibit intense room temperature phosphorescence arising mainly from the metal–alkynyl cluster cores. However, it has been noted that formation of the simple alkynyl dimers (RC<sub>2</sub>Au)*PP*(AuC<sub>2</sub>R) (*PP* = diphosphine) without metal–metal contacts in some cases also causes a visible increase in the emission intensity. As the Au(1) complexes with PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>PPh<sub>2</sub> ligands (*n* = 1–3) were reported earlier and show rather weak luminescence,<sup>17,21,22</sup> we decided to employ a family of alkynyl-arene based diphosphines, PPh<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>C<sub>2</sub>PPh<sub>2</sub> (*n* = 0–3) for the preparation as well as detailed photophysical and theoretical studies of their bimetallic gold(1) alkynyl derivatives.

# Experimental

## General comments

Au(tht)Cl (tht = tetrahydrothiophene),<sup>23</sup> (AuC<sub>2</sub>R)<sub>*n*</sub> (R = Ph, Bu')<sup>24</sup> were obtained according to literature methods. The diphosphines

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<sup>†</sup> Electronic supplementary information (ESI) available: X-ray crystallographic data for **6**, optimized Cartesian coordinates of **1–3**. CCDC reference number 838558. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11494h

 $PPh_2C_2(C_6H_4)_nC_2PPh_2$  (n = 0 (L0), 1 (L1), 2 (L2), 3 (L3)) were prepared as previously reported.<sup>19,20,25</sup> Other reagents and solvents were used as received. The solution 1D <sup>1</sup>H, <sup>31</sup>P NMR and <sup>1</sup>H-<sup>1</sup>H COSY spectra were recorded on a Bruker Avance 400 spectrometer. Microanalyses were carried out in the analytical laboratory of the University of Eastern Finland.

# (AuC<sub>2</sub>CH<sub>2</sub>O-Bu<sup>t</sup>)<sub>n</sub>

Au(tht)Cl (200 mg, 0.624 mmol) was suspended in acetone (10 ml), followed by HC<sub>2</sub>CH<sub>2</sub>O-Bu' (72 mg, 0.0642 mmol) and NEt<sub>3</sub> (65 mg, 0.644 mmol). The suspension became a transparent paleyellow solution, which was stirred for 20 min in the absence of light. Addition of water (15 ml) caused precipitation of a flaky pale solid that was collected by centrifugation, washed with water (3 × 5 ml) and vacuum dried to give crude  $(AuC_2CH_2O-Bu')_n$ of sufficient purity, which was used in further synthesis without additional purification (158 mg, 82%).

# $(AuC_2Ph)_2PPh_2C_2C_2PPh_2$ (1)

 $(AuC_2Ph)_n$  (100 mg, 0.336 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and PPh<sub>2</sub>C<sub>2</sub>C<sub>2</sub>PPh<sub>2</sub> (72 mg, 0.172 mmol) was added, and the yellow suspension turned into a yellowish solution within minutes. It was then stirred for 10 min in the absence of light, concentrated to *ca.* 3 ml, filtered and precipitated by slow addition of an excess of hexanes (10 ml). Beige crystalline material was washed with diethyl ether and vacuum dried (153 mg, 90%). **1** is of limited stability in solution at room temperature as the nearly colorless solution of this complex rapidly darkens. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>;  $\delta$ ): 18.0 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ ): 7.78 (dd, 8H, *ortho*-H (Ph–P), *J*(HH) 7.6, *J*(PH) 14.1 Hz), 7.57–7.45 (m, 16H), 7.28–7.19 (m, 6H). Anal. Calc. for Au<sub>2</sub>C<sub>44</sub>H<sub>30</sub>P<sub>2</sub>: C, 52.09; H, 2.98. Found: C, 51.71; H, 3.22.

## $(AuC_2Ph)_2PPh_2C_2C_6H_4C_2PPh_2$ (2)

 $(AuC_2Ph)_n$  (75 mg, 0.252 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and PPh<sub>2</sub>C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>PPh<sub>2</sub> (64 mg, 0.130 mmol) was added, and the yellow suspension turned into a yellowish solution within minutes. It was stirred for 30 min in the absence of light, treated with activated charcoal, passed through a layer of Al<sub>2</sub>O<sub>3</sub> (neutral, 0.5 × 3 cm), concentrated to *ca*. 5 ml, and precipitated by addition of an excess of hexanes (15 ml). Colorless crystalline material was washed with diethyl ether and vacuum dried (125 mg, 91%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>;  $\delta$ ): 16.2 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ ): 7.86 (dd, 8H, *ortho*-H (Ph–P), *J*(HH) 8.1, *J*(PH) 14.2 Hz), 7.61 (s, 4H, =-C<sub>6</sub>H<sub>4</sub>-=), 7.54–7.47 (m, 16H), 7.28–7.19 (m, 6H). Anal. Calc. for Au<sub>2</sub>C<sub>50</sub>H<sub>34</sub>P<sub>2</sub>: C, 55.06; H, 3.14. Found: C, 55.02; H, 3.43.

# $(AuC_2Ph)_2PPh_2C_2(C_6H_4)_2C_2PPh_2$ (3)

Prepared analogously to **2** using PPh<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>PPh<sub>2</sub>. Pale yellowish crystalline material (89%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>;  $\delta$ ): 16.0 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ ): 7.88 (dd, 8H, *ortho*-H (Ph–P), *J*(HH) 8.0, *J*(PH) 14.2 Hz), 7.66 (AB system  $\equiv$ C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>- $\equiv$ , 8H), 7.55–7.47 (m, 16H), 7.28–7.19 (m, 6H). Anal. Calc. for Au<sub>2</sub>C<sub>56</sub>H<sub>38</sub>P<sub>2</sub>: C, 57.64; H, 3.28. Found: C, 57.30; H, 3.57.

#### $(AuC_2Ph)_2PPh_2C_2(C_6H_4)_3C_2PPh_2$ (4)

Prepared analogously to **2** using PPh<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C<sub>2</sub>PPh<sub>2</sub>. Pale yellow crystalline material (88%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>;  $\delta$ ): 16.0 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ ): 7.89 (dd, 8H, *ortho*-H (Ph–P), *J*(HH) 8.1, *J*(PH) 14.2 Hz), 7.72 (s, =-C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>-==, 4H), 7.69 (s (coalesced AB system), ==-C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>-==, 8H), 7.55–7.47 (m, 16H), 7.28–7.19 (m, 6H). Anal. Calc. for Au<sub>2</sub>C<sub>62</sub>H<sub>42</sub>P<sub>2</sub>: C, 59.92; H, 3.41. Found: C, 59.79; H, 3.74.

#### $(AuC_2-Bu')_2PPh_2C_2(C_6H_4)_3C_2PPh_2$ (5)

 $(AuC_2Bu)_n$  (50 mg, 0.180 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and  $PPh_2C_2(C_6H_4)_3C_2PPh_2$  (60 mg, 0.93 mmol) was added, and the vellow suspension turned into a nearly colorless solution within minutes. It was stirred for 30 min in the absence of light, treated with activated charcoal, passed through a layer of Al<sub>2</sub>O<sub>3</sub> (neutral,  $0.5 \times 3$  cm), concentrated to *ca*. 1 ml and diluted with ethanol (5 ml) to give an opaque solution, in which crystalline needles started to form. Then more ethanol (5 ml) was added followed by hexanes (10 ml). The pale crystalline solid was additionally recrystallized by slow evaporation of a dichloromethane-ethanol solution of 5 at 5 °C. Colorless crystalline material (98 mg, 91%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>; δ): 16.3 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>; δ): 7.95 (dd, 8H, ortho-H (Ph–P), J(HH) 7.9, J(PH) 14.0 Hz), 7.78 (s, =-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<s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 $\equiv$ , 4H), 7.75 (s (coalesced AB system),  $\equiv$ -C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>- $\equiv$ , 8H), 7.59-7.51 (m, 12H), 1.27 (s, t-Bu, 18H). Anal. Calc. for Au<sub>2</sub>C<sub>58</sub>H<sub>50</sub>P<sub>2</sub>: C, 57.91; H, 4.19. Found: C, 57.59; H, 4.30.

# $(AuC_2CH_2O-Bu')_2PPh_2C_2(C_6H_4)_3C_2PPh_2$ (6)

Prepared analogously to **2** using  $(AuC_2CH_2O-Bu')_n$  and PPh<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C<sub>2</sub>PPh<sub>2</sub>. Recrystallized by slow evaporation of a dichloromethane–hexane solution of **6** at 5 °C. Colorless crystalline material (86%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>;  $\delta$ ): 15.8. <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ ): 7.86 (dd, 8H, *ortho*-H (Ph–P), *J*(HH) 8.0, *J*(PH) 14.2 Hz), 7.72 (s, 4H, =-C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>-==), 7.69 (s (coalesced AB system), =-C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>-=, 8H), 7.56–7.46 (m, 12H), 4.26 (s, CH<sub>2</sub>, 4H), 1.27 (s, *t*-Bu, 18H). Anal. Calc. for Au<sub>2</sub>C<sub>60</sub>H<sub>54</sub>O<sub>2</sub>P<sub>2</sub>: C, 57.06; H, 4.31. Found: C, 56.65; H, 4.53.

# $(AuCl)_2PPh_2C_2(C_6H_4)_3C_2PPh_2$ (7)

Au(tht)Cl (100 mg, 0.312 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and PPh<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C<sub>2</sub>PPh<sub>2</sub> (101 mg, 0.156 mmol) was added, and the nearly colorless solution was stirred for 30 min and evaporated. The pale residue was washed with diethyl ether (2 × 6 cm<sup>3</sup>) and recrystallized by slow evaporation of a dichloromethane–hexane solution of **7** at 5 °C. Colorless crystalline material (154 mg, 89%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>;  $\delta$ ): 3.1 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ ): 7.87 (dd, 8H, *ortho*-H (Ph–P), *J*(HH) 7.6, *J*(PH) 15.0 Hz), 7.73 (s, 4H, =-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-=, 8H), 7.50–7.59 (m, 12H). Anal. Calc. for Au<sub>2</sub>C<sub>46</sub>Cl<sub>2</sub>H<sub>32</sub>P<sub>2</sub>: C, 49.71; H, 2.90. Found: C, 49.79; H, 2.96.

**Photophysical measurements.** Steady-state absorption and emission measurements in solution were recorded on a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorometer, respectively. Both the wavelength-dependent excitation and emission response of the fluorometer have been calibrated. To determine the photoluminescence quantum yield in solution,

the samples were degassed by three freeze-pump-thaw cycles. Quinine sulfate monohydrate in sulfuric acid and 7-azaindole in cyclohexane, with quantum yields of ~0.57<sup>26</sup> and ~0.22,<sup>27</sup> respectively, served as the standard for measuring the quantum yield. Nanosecond lifetime studies were performed with an Edinburgh FL 900 photon-counting system using a hydrogen-filled lamp as the excitation source. The emission decays were fitted by the sum of exponential functions with a temporal resolution of ~300 ps via the deconvolution of instrument response function. Nanosecondpicosecond lifetime studies were performed with an Edinburgh OB 900-L time-correlated single photon counting system coupled with a femtosecond Ti-Sapphire oscillator (80 MHz, Spectra-Physics) coupled with a regenerative amplifier (Spitfire Pro, Spectra-Physics) that produces 120 fs laser pulses at 800 nm with 1 kHz repetition rate, and then used to produce the second harmonic (400 nm). A polarizer was placed in the emission path to ensure that the polarization of the fluorescence was set at the magic angle  $(54.7^{\circ})$  with respect to that of the pump laser to eliminate the fluorescence anisotropy. The resolution of the TCSPC system is limited by the detector response of ~50 ps. The fluorescence decays were analyzed by the sum of exponential functions with an iterative convolution method which allows partial removal of the instrument time broadening and consequently renders a temporal resolution of ~30 ps.

The phosphorescence lifetime (> $\mu$ s) was then detected by an optical spectrum analyzer, consisting of an intensified chargecoupled device (ICCD) with detector control (PI-MAX, Princeton Instruments) in conjunction with a monochromator (SP2300i, Acton). The gate channel of the ICCD was open at 50 ns and synchronized with the firing time of the excitation pulse. Typically, the second harmonic (400 nm, fwhm <20 ns) of a Nd:YAG pumped Ti:sapphire laser (LT-2211, LOTIS TII) was used as the excitation pulse. For the higher energy excitation at *e.g.* 340 nm, a traveling-wave optical parametric amplifier of whitelight continuum (TOPAS-C, Spectra Physics) was driven by the fundamental of the above mentioned regenerative amplifier. The output of TOPAS-C produced NIR signal beam (1150–1560 nm, 1 kHz, 80  $\mu$ J) was selected as 1360 nm and then used to produce the fourth harmonic (340 nm) as an excitation source.

The femto-picosecond transient absorption measurements were performed according to previous reports.28 However, the system has been modified to improve the sensitivity and stability. In brief, a Spitfire Pro system (Spectra-Physics) was used as the laser source. This system comprises a seed laser, a pump laser, a stretcher, a Ti:sapphire regenerative amplifier and a compressor. The output of the system consists of pulses of 800 nm, 1 W, 120 fs (fwhm) at a repetition rate of 1 kHz. The pump-probe spectroscopic setup is mainly based on an ExciPro spectrometer (CDP System Corp). The Spitfire Pro output is first split (50%) into two beams, in which the pump is converted to designated excitation wavelengths by coupling it into a third-harmonic generator (for 266 nm excitation). The probe beam is first passed through a computer-controlled delay line, and then focused on a 1 mm thick sapphire plate to generate a white light continuum (350–1000 nm). The pump beam is then passed through a computer controlled optical chopper, and focused (3 mm) onto the sample cell. The sample cell is a 1 mm optical path quartz cylindrical cell placed in a variable speed rotating holder. The white light probe beam is collimated and focused into the sample cell, superimposed to

the pump beam at an angle of about 5 degrees. To minimize the temporal chirp in the spectrum, parabolic mirrors are used for focus and collimation. After passing through the sample cell, the white continuum is coupled into a 100  $\mu$ m optical fiber connected to a diode array. Typically, time-resolved absorption spectra were acquired averaging over 200 excitation pulses at any delay time. With 120 fs pump and probe pulses, the effective time resolution of the ultrafast spectrometer that is, the risetime of an "instantaneous" signal, is about 220 fs.

X ray structure determination. The crystal of 6 was immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data was collected on a Bruker Kappa ApexII diffractometer using Mo-Ka radiation  $(\lambda = 0.71073 \text{ Å})$ . The APEX2<sup>29</sup> program package was used for cell refinements and data reduction. The structure was solved by direct methods using the SIR97<sup>30</sup> program with the WinGX<sup>31</sup> graphical user interface. The absorption effects were corrected by semiempirical methods based on equivalent reflections (SADABS).<sup>32</sup> Structural refinements were carried out using SHELXL-97.33 The Au molecule is located around the center of symmetry, and the asymmetric unit contains half of the Au molecule. Both the hexane and dichloromethane of crystallization are disordered over two sites with occupancy ratios of 0.51/0.49 and 0.57/0.43. The C-C and C-Cl distances in these molecules were restrained. Similarly, the heavy atoms in these solvent molecules were restrained so that their U<sub>ii</sub> components approximate to isotropic behavior. The O-<sup>t</sup>Bu units were also slightly disordered but no disorder model was used in the final refinement. The hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.95–0.99 Å and  $U_{iso} = 1.2-1.5 \cdot U_{eq}$  (parent atom). The crystallographic details are summarized in the corresponding footnote.<sup>†</sup>

Computational details. The studied structures were investigated with the Second-Order Approximate Coupled-Cluster method (CC2), which is an approximation of the Coupled Cluster Singles and Doubles (CCSD) method.<sup>34</sup> All atoms were described by a triple-valence-zeta quality basis set with polarization functions (def2-TZVP for Au, def-TZVP for other elements).35 Scalar relativistic effects were taken into account by employing a 60-electron relativistic effective core potential for gold.<sup>36</sup> The resolution-of-the-identity technique was used to speed up the calculations.37 The studied complexes can rotate freely around the P-C<sub>2</sub>-(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>-C<sub>2</sub>-P axis and we utilized  $C_{2h}$  point group symmetry to speed up calculations (utilizing  $C_{2v}$  point group symmetry yielded the same results). The geometries of the ground and excited states were fully optimized at the RI-CC2/TZVP level of theory using the TURBOMOLE program package (versions 6.2 and 6.3).<sup>38</sup> Additional electronic structure analyses were carried out using the AOMix program package.39

<sup>‡</sup> Crystal data for 6: C<sub>130</sub> H<sub>130</sub>Au<sub>4</sub>Cl<sub>8</sub>O<sub>4</sub>P<sub>4</sub>, *M* = 2951.69, yellow needle, 0.29 ×0.11 × 0.09 mm<sup>3</sup>, triclinic, space group P<sub>1</sub> *a* = 11.6702(9), *b* = 13.6745(11), *c* = 21.1659(17) Å, *α* = 97.135(3), *β* = 103.103(2), *γ* = 93.052(2)°, *V* = 3252.7(4) Å<sup>3</sup>, *Z* = 1, *D<sub>c</sub>* = 1.507 g cm<sup>-3</sup>, *F*<sub>000</sub> = 1454, Mo-Kα radiation, *λ* = 0.71073 Å, *T* = 100(2)K, 2*θ*<sub>max</sub> = 52.0°, 32.989 reflections collected, 12.098 unique (*R*<sub>int</sub> = 0.0324). Final *GooF* = 1.074, *RI* = 0.0569, *wR2* = 0.1331, *R* indices based on 12.098 reflections with *I* > 2*σ*(*I*) (refinement on *F*<sup>2</sup>), 708 parameters, 212 restraints; *wR2* = 0.1558 (all data).

#### **Results and discussion**

#### Synthesis and characterization

Reactions of the polymeric gold(I) phenylacetylide with a family of diphosphine ligands  $PPh_2-C_2-(C_6H_4)_n-C_2-PPh_2$  (*n* = 0 (L0), 1 (L1), 2 (L2), 3 (L3)) result in clean and high yield formation of the corresponding bimetallic complexes (PhC<sub>2</sub>Au)PPh<sub>2</sub>-C<sub>2</sub>- $(C_6H_4)_n - C_2 - PPh_2(AuC_2Ph)$  (n = 0 (1), 1 (2), 2 (3), 3 (4)), depicted in Scheme 1. Analogously, treatment of the  $(AuC_2Bu')_n$  and  $(AuC_2CH_2OBu')_n$  acetylides with PPh<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C<sub>2</sub>PPh<sub>2</sub> diphosphine gave the dimeric compounds 5 and 6, which are similar to 4. This depolymerization methodology is a general and well documented synthetic approach, leading to a variety of gold alkynyl complexes.<sup>9,22,24</sup> In the obtained species the phosphine ligands bridge two Au<sup>I</sup> centers, which evidently demonstrates two-coordinate linear geometry, typical for the alkynyl-phosphine compounds.<sup>8,9,11,22</sup> The reaction of the labile Au(tht)Cl precursor with L3 ligand gave a chloro-gold(I) diphosphine complex  $(ClAu)PPh_2-C_2-(C_6H_4)_n-C_2-PPh_2(AuCl)$  in high yield (Scheme 1).



Scheme 1 Synthesis of the complexes 1–7:  $CH_2Cl_2$ , 298 K, 30 min, yields 86-91% (P = PPh<sub>2</sub>).

The solid-state structure of complex **6** has been determined by an X-ray diffraction study (Fig. 1). The rest of the complexes (1-5, 7) were characterized by NMR spectroscopic studies and elemental analyses. The <sup>31</sup>P NMR spectra of **1–6** display singlet resonances in the region 15.8–18 ppm, while a high field signal at 3.1 ppm is observed for **7**. The detected low field shift in comparison to the free phosphine ligands unambiguously indicates the coordination of the P donor atoms to the gold(1) ions.

Assignment of the proton NMR spectra of complexes 1–7 has been confirmed by the comparative analysis of their spectral



Fig. 1 Structural plot of the complex  $(AuC_2CH_2OBu')_2PPh_2C_2(C_6H_4)_3-C_2PPh_2$  (6). Selected interatomic distances (Å) are: Au(1)–C(47) 1.996(11), Au(1)–P(1) 2.276(2), Au(1)–Au(2) 3.1287(5), Au(2)–C(54) 1.992(14), Au(2)–P(2) 2.262(3).

patterns with those of the recently reported Au<sup>I</sup>–Ag<sup>I</sup> compounds based on these diphosphines.<sup>20</sup> The amount of the signals observed together with their multiplicity and relative intensities completely match the proposed structures and indicate that these compounds exist in their molecular forms in solution.

X-ray diffraction analysis of complex **6** revealed a dimeric structure, in which two molecules are linked together by aurophilic interactions (Fig. 1). A similar structural motif was observed in analogous gold complexes based on the 1,4-bis(diphenylphosphino)benzene or 1,2-bis(diphenylphosphino)ethane ligands.<sup>2,21</sup> Solution NMR spectroscopic data (see Experimental) correspond to the symmetrical monomolecular form of **6**, indicating dissociation of the Au–Au bonds in fluid medium.<sup>21</sup>

#### **Photophysical properties**

Fig. 2 and 3 show absorption and emission spectra of complexes 1– 7 and ligand L3 (see Scheme 1 for the structures) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Solid-state emission spectra at room temperature are shown in Fig. S1, ESI.<sup>†</sup> Note that the separation into two figures is mainly to avoid spectral congestion. Based on the theoretically determined photophysical characteristics (*vide infra*), the lowest lying absorption in the singlet manifold for 1–3 is ascribed to a combination of the intraligand  $\pi \rightarrow \pi^*$  of both  $\pi$ -conjugated C=C-Ar and PPh<sub>2</sub>C=C(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>C=CPPh<sub>2</sub>



**Fig. 2** UV/vis absorption and normalized emission spectra of 1–4 in degassed CH<sub>2</sub>Cl<sub>2</sub> at room temperature,  $\lambda_{\text{excit}} = 300$  nm for 1–3,  $\lambda_{\text{excit}} = 330$  nm for 4.



**Fig. 3** UV/vis absorption and normalized emission spectra of **5–7** in degassed CH<sub>2</sub>Cl<sub>2</sub> and **L3** in aerated CH<sub>2</sub>Cl<sub>2</sub> at room temperature,  $\lambda_{excit} = 330$  nm for **5–7**,  $\lambda_{excit} = 300$  nm for **L3**. Inset: the enlargement of spectrum of **5–7** in the region of 530–700 nm. Note that no phosphorescence can be resolved from emission of **L3**.

(n = 0-2) ligands and their cross excitation, *i.e.* the interligand  $\pi \rightarrow \pi^*$  transitions of the alkynyl and phenyl moieties, mixed with a minor percentage of Au(I)-to-alkyne metal-to-ligand charge transfer (MLCT) transition.

As for 4–7, the lowest lying transition is dominated by intraligand  $\pi \rightarrow \pi^*$  of the PPh<sub>2</sub>C $\equiv$ C(C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C $\equiv$ CPPh<sub>2</sub> chromophore, whereas the contribution of MLCT is virtually zero (*vide infra*). The pure  $\pi \rightarrow \pi^*$  allowed transition is manifested in the fact that complexes 5–7 exhibit similar absorption peaks at 330 nm, despite their possessing different R-terminated alkynyl groups and chloride (see Scheme 1), with  $\varepsilon$  as high as  $\geq 10^5$  cm<sup>-1</sup> M<sup>-1</sup>. This assignment is consistent with the previous reports on the relevant alkynyl analogues, for which the dominant absorption band in the spectral region of 250–320 nm is ascribed to the characteristic band of the alkynyl-phosphine moieties.<sup>21,22,40</sup> Further confirmation is given by the absorption spectrum of ligand L3 (PPh<sub>2</sub>C $\equiv$ C(C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C $\equiv$ CPPh<sub>2</sub>), which exhibits nearly identical spectral features with respect to those of complexes 5–7 (Fig. 3).

The above trend of transition character can be rationalized by the increase of  $\pi$ -conjugation from n = 0 to n = 3 of the ligands PPh<sub>2</sub>C=C(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>C=CPPh<sub>2</sub>, such that its corresponding HOMO (LUMO) is increased (decreased). Conversely, the metal (Au(I)) d<sub>π</sub> orbital energy is virtually insensitive to the  $\pi$ -elongation. As a result, for the titled complexes 1–7, the % contribution of the metal  $d_{\pi}$  orbital to the HOMO is expected to be decreased upon increasing *n* from 0 to 3. Up to n = 3, the  $d_{\pi}$  energy is substantially lower than that of the  $\pi$  orbital, giving null contribution of the  $d_{\pi} \rightarrow \pi^*$  transition, *i.e.*, no MLCT contribution to the lowest lying transition.

The viewpoint of the lowest lying transition having a small %MLCT character in 1–3 (<5%) and ~0% MLCT character in 4–7 is firmly supported by the observed emission properties. In this study, particular attention is paid to the observation of dual emission for all titled compounds. Evidently, as shown in Fig. 2, complexes 1–3 exhibit very distinct dual emission consisting of fluorescence and phosphorescence in the short and long wavelength regions, respectively. The classification of each is based on the associated radiative decay rate constant ( $k_r$ ), for which the fluorescence and phosphorescence are in the range of 10<sup>7</sup>–10<sup>9</sup> s<sup>-1</sup> and «10<sup>5</sup> s<sup>-1</sup>, respectively (see Table 1).

Moreover, as shown by quantum yield data (Table 1), the longer wavelength emission band is drastically quenched by the presence of  $O_2$  (in aerated solution). Thus, its assignment to the phosphorescence seems to be unambiguous, which, in theory, is quenched by O<sub>2</sub> via a well established mechanism associated with collisionally induced energy transfer.<sup>41</sup> Extending to n = 3, complex 4 exhibits an intense fluorescence band with a maximium at ~375 nm, accompanied by a rather weak phosphorescence maximized at ~550 nm in degassed CH<sub>2</sub>Cl<sub>2</sub> solution. Complexes 5 and 6, which are close relatives of 4 having the phenyl groups in R positions replaced by t-butyl, 2-methoxy-2-methylpropyl (see Scheme 1), respectively, and 7 possessing chloride ligands instead of the alkynyl ones, also exhibit similar dual emission peaks with fluorescence being dominant. In fact, for complexes 5-7, spectral enlargement is necessary in order to resolve the obscure phosphorescence in degassed solution (see inset of Fig. 3). In contrast to the polymetallic Au(I) containing clusters,<sup>20,42</sup> phosphorescence emission of the titled bimetallic complexes 1-7 is drastically quenched by triplet molecular oxygen, an inherent feature of many luminescent coordination transition metal complexes.<sup>43</sup> This is apparently due to the unprotected Au(I)-alkyne chromophores in the bimetallic complexes, which are exposed to the surrounding solvents in which O<sub>2</sub> molecules are dissolved.

Table 1 Photophysical properties of the Au(I) complexes 1-7 and ligand (L3) in CH<sub>2</sub>Cl<sub>2</sub>

	$\lambda_{ab}/nm (10^{-4} \ \epsilon/cm^{-1} \ M^{-1})$	$\lambda_{em}/nm$	$\Phi^a$	$\Phi^b$	$ au_{ m obs}/ m ns^c$	$ au_{ m obs}/\mu{ m s}^d$	$k_{\rm r}/{ m s}^{-1},$
1	286(2.0), 302sh(1.4)	394, 455	0.0003 [fl], 0	0.0003 [fl], 0.0017	0.013	0.88	$1.30 \times 10^7$ [fl], $1.93 \times 10^3$
2	272sh(1.8), 283(2.1), 294(2.4), 312(2.2)	370, 482, 517	0.001 [fl], 0	0.001 [fl], 0.006	0.020	73	$5.00 \times 10^7$ [fl], 82.2
3	271(3.9), 285(4.7), 299sh(4.8), 315 (5.6)	352, 370, 528, 570	0.077 [fl], 0	0.077 [fl], 0.023	0.050	296	$1.57 \times 10^{9}$ [fl], 77.7
4	271(4.1), 285(4.8), 325 (7.0)	375, 394, 549, 591	0.4 [fl], 0	0.4 [fl], 0.02	0.45	680	$2.68 \times 10^{9}$ [fl], 29
5	325(12.6)	375, 392, 550, 593	0.99 [fl], 0	0.99 [fl], <0.01	0.66	1175	$1.52 \times 10^{9}$ [fl]
6	325(11.8)	375, 393, 547, 595	0.93 [fl], 0	0.93 [fl], 0.01	0.55	1322	$1.70 \times 10^{9}$ [ff], 7.6
7	277sh(3.6), 327(5.9)	375, 394 550, 593	0.99 [fl], 0	0.99 [fl], < 0.01	0.58	2300	$1.72 \times 10^{9}$ [fl],
L3	328(5.7)	372, 386	0.002 [fl]	0.002[fl]	0.87		$2.3 \times 10^{6}$ [f]

<sup>*a*</sup> Measured in aerated CH<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup> Measured in degassed CH<sub>2</sub>Cl<sub>2</sub>. <sup>*c*</sup>  $\tau_{obs}$  denotes the lifetime of the S<sub>1</sub> state, which is resolved by pico-femtosecond transient absorption for 1–3 and by fluorescence time-correlated single photon counting measurement for 4–7. <sup>*d*</sup>  $\tau_{obs}$  denotes the lifetime of the phosphorescence band. <sup>*e*</sup>  $k_r$  are deduced from data obtained in the fluorescence and phosphorescence band. Information regarding the fluorescence band is marked with [fl]. 7-Azaindole in cyclohexane ( $\lambda_{excit}$  = 300 nm for 1–3 and L3) and quinine sulfate monohydrate in sulfuric acid ( $\lambda_{excit}$  = 330 nm for 4–7) were used as standards for the quantum yield ( $\Phi$ ) measurements, respectively.

For complexes 1-4, in which the only structural difference lies in the number (n) of the phenylene rings in the spacer of the bridging diphosphine, the peak wavelengths for both fluorescence and phosphorescence are progressively red shifted with an increase in *n* from 0 to 3. The results are in accordance with computational results, concluding that the LUMO is mainly located at the diphosphine ligands  $PPh_2-C_2-(C_6H_4)_n-C_2-PPh_2$  (n = 0-3) for both singlet and triplet manifolds. Thus, upon increasing the number of phenvlene rings from n = 1 to n = 3, the  $\pi$ -conjugation. in part, is expected to be increased, resulting in a decrease of the lowest lying transition gap.<sup>20,21</sup> For 4-7, similar spectral features (peak wavelength and profile) for both fluorescence and phosphorescence are in accordance with computational studies. For n = 3, the HOMO and LUMO are predominantly  $\pi$  and  $\pi^*$  in character, respectively, and are located over the PPh<sub>2</sub>-C<sub>2</sub>-(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>-C<sub>2</sub>-PPh<sub>2</sub> ligand moiety.

Despite the fact that most Au(1) homometallic phosphine compounds demonstrate solely phosphorescence emission,<sup>4,10,22,44</sup> complexes 1–7, especially 4–7, exhibit high fluorescence quantum yields. The dominant fluorescence suggests a relatively slow  $S_1 \rightarrow T_m$  ( $m \ge 1$ ) intersystem crossing rate so that the  $S_1 \rightarrow S_0$  fluorescence radiative decay is able to compete and even dominate. To simplify the approach, we assume that the intersystem crossing takes place solely *via* the  $S_1 \rightarrow T_1$  pathway. The corresponding rate constant,  $k_{isc}$ , is then expressed as

$$k_{\rm isc} \propto \frac{\langle \Psi_{\rm T_l} | H_{\rm SO} | \Psi_{\rm S_l} \rangle^2}{(\Delta E_{\rm S_l} - T_{\rm l})^2}$$
(1)

where  $H_{so}$  is the Hamiltonian for spin-orbit coupling (SOC), and  $\Delta E_{S_1-T_1}$  is the energy difference between  $S_1$  and  $T_1$  states. Since the metal  $d_{\pi}$  orbital is directly coupled into the spin-orbit coupling matrix, the rate of  $S_1 \rightarrow T_1$  intersystem crossing should be greatly influenced as well as enhanced by those low lying transitions incorporating a metal  $d_{\pi}$  orbital,<sup>45</sup> the result of which can be defined as an internal heavy atom effect. Conversely, for the lack of MLCT and hence no  $d_{\pi}$  contribution, the coupling matrix should be rather small. In this case the Au(I) atom simply executes an external heavy atom effect, which is qualitatively proportional to  $Z^{8}/r^{6}$  (Z: the atomic number, r: distance between the metal atom and the center of the chromophore for the transition), if Au(I) is treated as a hydrogen-like atom via an oversimplified approach. Standing on this basis, the above spectral properties can be rationalized by the rather small %MLCT or even zero MLCT contribution to the lowest lying transition (vide infra) for the titled complexes. Since the metal  $d_{\pi}$  orbital in *e.g.* 4–7 is not directly involved in the transition, Au(I) only executes the external heavy atom effect rather than the internal heavy atom effect,<sup>46</sup> giving rise to a small  $k_{isc}$ , and hence the dominant fluorescence. In general, similar regularities have been observed in solid-state emission spectra of the complexes 2-7 (Fig. S1, ESI, † the emission of 1 was too weak to be resolved). Compounds 2, 3 and 4 exhibit dual emission (fluorescence and phosphorescence) while dominant fluorescence was recorded for 5-7. This indicates that there is no drastic difference in the intersystem crossing in solid, and potential Au-Au intermolecular interactions (in fact determined for complex 6, Fig. 1) should have a negligible effect on the emission parameters. To gain further insight into the relaxation dynamics, we also carried out the pico-femtosecond UV/Vis

transient absorption spectroscopy (see Experimental section for detail). Using complex **3** as an example, the results shown in Fig. 4 clearly indicate an instant rise of the absorption peak at ~585 nm after 266 nm (~120 fs pulse width) excitation in  $CH_2Cl_2$ . The 585 nm transient absorption then gradually decreases following a single exponential decay (see Fig. 5) with a time constant of 50 ps (monitored at 617 nm). The decay of the 585 nm absorbance is simultaneously accompanied by the rise of an absorption band with a maximum at ~510 nm.



Fig. 4 Femtosecond transient absorption spectra of 3 in CH<sub>2</sub>Cl<sub>2</sub> measured following excitation at 266 nm.



Fig. 5 Relaxation dynamics of transient absorption for 3 in  $CH_2Cl_2$  excited at 266 nm (~120 fs), monitored at 617 nm (black line) and 500 nm (blue line). The red line is the fit of the experimental data with an exponential function.

The 510 nm transient exhibits dual rise time, which is fitted to be the system response limit (<250 fs) and 48 ps (monitored at 500 nm). The latter component, within experimental/fitting error, is well correlated with the decay of the 585 nm transient absorbance. The former system-response-limited rise component can be rationalized by the overlap between rise and decay of the 510 nm and 585 nm bands, respectively. It is thus reasonable for us to assign the 585 nm and 510 nm absorption bands originating from the  $S_1 \rightarrow S_n$  and  $T_1 \rightarrow T_m$  transient absorptions, respectively, which have a precursor-successor type of relationship. Assuming

	$\lambda_{ab} \ S_0 \rightarrow S_1 \ (nm)$		$\lambda_{ab}\;S_{0}\rightarrow S_{2}\;(nm)$		$\lambda_{\rm em} \; { m S}_{ m l}  ightarrow { m S}_{ m 0} \; ({ m nm})$		$\lambda_{em} \; T_{\scriptscriptstyle 1} \to S_{\scriptscriptstyle 0} \; (nm)$	
	Theor."	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
1	310 (1.04)	302	266 (0.15)	28Ĝ	387	394	392	45Ŝ
2	306 (1.01)	312	274 (1.59)	294	397	370	518	517
3	311 (2.42)	315	293 (0.79)	299	363	370	550	570
4	325 (3.35)	325	295 (0.45)	285	378	394	564	591
5	325 (3.19)	325	_ ` `		377	392	565	593
6	324 (3.29)	325			376	393	565	595
7	333 (3.16)	327	247 (0.03)	277	386	394	569	593
L3	325 (3.03)	328	_ ` `		378	386		
" Wavel	engths in nm_oscillat	or strengths giv	en in parentheses		570	500		

 Table 2
 Computational photophysical results for the clusters 1–7 and the ligand L3 (CC2/TZVP level of theory)

that the rate of  $S_1 \rightarrow T_1$  intersystem crossing dominates the decay of the  $S_1$  state, the rate constant of the intersystem crossing is thus determined to be ~(50 ps)<sup>-1</sup> equivalent to  $2.0 \times 10^{10}$  s<sup>-1</sup>. A similar procedure is applied for complexes 1 and 2 and the resulting time constant of intersystem crossing is indicated by the inverse of the observed fluorescence lifetimes (Table 1), which are deduced to be  $7.7 \times 10^{10}$  s<sup>-1</sup> and  $5.0 \times 10^{10}$  s<sup>-1</sup>, respectively. As for 4-7, the rate of intersystem crossing is apparently much slower, so that a time-correlated single photon counting technique was applied to resolve the lifetime of fluorescence (Table 1). Note that the rate of intersystem crossing for 4-7 should be slower than  $1/\tau^{f}_{obs}$ , where  $\tau^{f}_{obs}$  is the observed lifetime of the fluorescence. As a result, the data shown in Table 1 clearly indicates that the rate of intersystem crossing  $(1/\tau_{abs})$  for 4–7 is  $\sim 1-2 \times 10^9$  s<sup>-1</sup>, which is apparently smaller than that of 1-3 by more than one order of magnitude, consistent with the decrease of %MLCT in the lowest lying transition state in a qualitative manner.

#### **Computational studies**

We investigated the structural and photophysical characteristics of the Au(I) complexes 1-7 and the phosphine ligand L3 by using ab initio quantum chemical methods (CC2/TZVP level of theory). First, we optimized the structures at the S<sub>0</sub> ground state. Comparison of the interatomic distances in the optimized  $S_0$ ground state and the X-ray structure of the complex 6 showed the theoretical and experimental structures to be in good agreement: R(Au-C): 1.96 Å vs. 1.992-1.996 Å; R(Au-P): 2.26 Å vs. 2.262-2.276 Å;  $R(C_6H_4-C_6H_4)$ : 1.48 Å vs. 1.476–1.487 Å. Next, we determined the singlet excitation spectra of the structures at the optimized S<sub>0</sub> geometry. The calculated excitation features are listed in Table 2. The theoretical  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  excitation wavelengths are in good agreement with the experimental ones, in particular for the  $S_0 \rightarrow S_1$  transitions. The transition densities for the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  singlet excitations shown in Fig. 6 shed light on the absorption properties of the complexes 1-4. The transition densities for the complexes 5-7 and the ligand L3 are shown in the ESI.<sup>†</sup> As the number of the phenylene rings in the  $PPh_2-C_2-(C_6H_4)_n-C_2-PPh_2$  ligand increases, the contribution of the Au atoms and the alkynyl ligands to the  $S_0 \rightarrow S_1$  excitation decreases, and for the complex 4, the excitation is practically a pure  $\pi \to \pi^*$  excitation within the phosphine ligand. The singlet excitations of complexes 5-7 are very similar to complex 4, as can also be expected from the identical excitation wavelengths. The



Fig. 6 Transition densities for the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  singlet excitations of complexes 1–4 (CC2/TZVP level of theory, density isovalue 0.002 a.u.). During the transition, the electron density increases in the blue areas and decreases in the red areas.

 $\pi \rightarrow \pi^*$  character of the  $S_0 \rightarrow S_1$  excitation is also confirmed by investigation of the photophysical characteristics of the pure phosphine ligand L3 (see ESI† for details).

To determine the emission energies for both fluorescence and phosphorescence, we first optimized the structures of the  $S_1$ ,  $S_2$  and  $T_1$  excited states. The emission energies for the complexes were then determined at the optimized excited state geometries. The calculated wavelengths of the emission features are listed in Table 2. The predicted emission wavelengths are not as accurate as the predicted excitation energies, but their trends are still in agreement with the experimental values. The transition densities for the  $S_1 \rightarrow S_0$  and  $T_1 \rightarrow S_0$  emission characteristics of complexes **5–7** are very similar to those of complex **4** (see ESI† for details). For complex **4**, both the lowest energy singlet and triplet emissions are of  $\pi^* \rightarrow \pi$  type within the phosphine ligand, while for **2** and **3**, the Au atoms and alkynyl ligands also contribute to the singlet



Fig. 7 Transition densities for the  $S_1 \rightarrow S_0$  and  $T_1 \rightarrow S_0$  emissions of complexes 1–4 (CC2/TZVP level of theory, density isovalue 0.002 a.u.). During the transition, the electron density increases in the blue areas and decreases in the red areas.

 $S_1 \rightarrow S_0$  emissions, consistent with the experimental results (vide supra).

#### Conclusions

We have prepared a series of bimetallic alkynyl-phosphine gold(I) complexes using a family of the diphosphines  $PPh_2C_2(C_6H_4)_nC_2PPh_2$  (*n* = 0–3) with conjugated dialkynyl-arene bridging spacers. The detailed photophysical investigations of the novel compounds revealed dual emission at ambient temperature containing contribution from both fluorescence and phosphorescence in short and long wavelength regions, respectively. An increase of  $\pi$ -conjugation in the diphosphine ligands (from n =0 to n = 3) leads to domination by the fluorescence component and decrease of the low-energy phosphorescence band. Variation of the nature of the alkynyl ligand and even its change to chloride has very little effect on the emission characteristics. Analysis of these spectral data obtained supported by extensive computational studies allowed for a tentative explanation of the observed emission to originate mainly from the intraligand  $\pi \rightarrow \pi^*$ transitions of the dialkynyl-arene chromophore of the diphosphine ligand, while the contribution of the Au(I)-to-alkyne MLCT transition is minor and decreases with an increase in the number (*n*) of phenylene rings in  $PPh_2C_2(C_6H_4)_nC_2PPh_2$ . The prevailing fluorescence with maximum quantum yield of 99% points to the major role of the  $S_1 \rightarrow S_0$  fluorescence radiative decay and slow  $S_1$  $\rightarrow$  T<sub>m</sub> (m  $\ge$  1) intersystem crossing rate, which was deduced to be in the range of  $10^9 \text{ s}^{-1}-10^{10} \text{ s}^{-1}$ .

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