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# Luminescent heterometallic gold–copper alkynyl complexes stabilized by tridentate phosphine<sup>†</sup>

Julia R. Shakirova,<sup>*a*</sup> Elena V. Grachova,<sup>*a*</sup> Vladislav V. Gurzhiy,<sup>*a*</sup> Igor O. Koshevoy,<sup>*a,c*</sup> Alexei S. Melnikov,<sup>*b*</sup> Olga V. Sizova,<sup>*a*</sup> Sergey P. Tunik<sup>*a*</sup> and Antonio Laguna<sup>*d*</sup>

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The reactions between trinuclear gold complex tppmAu<sub>3</sub>Cl<sub>3</sub> (tppm = tris(diphenylphosphino)methane), arylacetylenes  $HC_2C_6H_4X$  and  $Cu^+$  under basic conditions result in formation of the heterometallic complexes [tppm(AuC\_2C\_6H\_4X)\_3Cu]<sup>+</sup>, X = H (1), COOMe (2), CN (3), OMe (4), NH<sub>2</sub> (5). These compounds belong to one structural motif and consist of the heterometallic {(AuC\_2C\_6H\_4X)\_3Cu} core stabilized by the tridentate phosphine. Compounds 1–5 were characterized by polynuclear NMR and IR spectroscopy, ESI-MS and single-crystal X-ray analysis. Luminescence properties of these complexes have been studied and revealed a substantial red shift of the emission maxima with the increase in the electron donicity of the alkynyl ligands substituents in the 550–680 nm range. The theoretical calculations of the electronic structures showed that variations of the substituents on the alkynyl ligands display very little effect on the molecular structural parameters but show appreciable influence on the orbital energies and luminescence characteristics of the compounds under study.

# Introduction

The metal–metal interactions of the d<sup>10</sup> ions of the coinage metals have been intensely investigated for more than two decades since the attraction between gold atoms was highlighted and defined as "aurophilicity"<sup>1</sup> which resulted in exponential growth of the experimental<sup>2,3</sup> and theoretical<sup>4</sup> interest in this topic and was particularly stimulated by the intriguing photophysical properties of gold compounds.<sup>5</sup> Development of gold(I) polymetallic chemistry naturally resulted in expansion into the area of gold-containing heterometallic complexes,<sup>6</sup> due to the successful demonstration that the presence of mixed metal–metal interactions between the closed-shell d<sup>10</sup> ions causes the perturbation of the electronic structures and dramatic changes in the photophysical properties.<sup>7</sup> Therefore special attention has been

St.-Petersburg, Russia. E-mail: stunik@inbox.ru;

<sup>d</sup>Departamento de Quimica Inorganica, Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain paid to heteronuclear coinage metal compounds as they were shown to be very effective luminophores exhibiting exceptionally intense room temperature emission.<sup>8-11</sup>

One of the ways to enhance the metal-metal contacts and to stabilize the polymetallic cluster core is to use bridging bi- or polydentate ligands with short bite angles, which are capable of bringing the interacting metal ions into close proximity, *i.e.* to provide interatomic distances shorter than the sum of van der Waals radii. This methodology has been widely employed in the synthesis of numerous phosphine-containing species due to the high Au(I) affinity toward the phosphorus donor atom. Thus, utilization of homo- or heterobidentate bridging phosphine ligands in the preparation of Au(I) complexes is well documented in the literature and exemplified by a variety of compounds of different nuclearity – from bimetallic dimers<sup>2,12</sup> to polymetallic clusters and large supramolecular aggregates.<sup>6,10,13-15</sup> Interestingly, the coordination chemistry of gold(1) based on tri- or polydentate phosphines is very limited,<sup>2</sup> despite their high templating potential in the construction of the molecular multimetallic assemblies. For example, intense phosphorescence has been reported for the linear chain structures<sup>16,17</sup> built on tri- and tetraphosphines; the oligoether functionalized tripodal alkynyl-phosphine gold(1) complex serves as a photoluminescent sensor for Mg<sup>2+</sup> ions;18 and the combination of flexible triphosphine with bridging sulfide has driven the aggregation of a crown-like  $Au_{18}$ macrocycle.19

Recently our research efforts have focused on the synthesis and photophysical studies of the bimetallic Au(1)–Cu(1) and Au(1)–Ag(1) alkynyl-phosphine clusters, which showed unprecedented photoemissive properties, such as very high quantum efficiency (up to 96%) and negligibly small effect of

<sup>&</sup>lt;sup>a</sup>St.-Petersburg State University, Department of Chemistry,

*Fax:* +7 812 4286939; *Tel:* +7 812 4284028

<sup>&</sup>lt;sup>b</sup>St.-Petersburg State University, Department of Physics, St.-Petersburg, Russia

<sup>&</sup>lt;sup>c</sup>University of Eastern Finland, Joensuu, 80101, Finland

<sup>&</sup>lt;sup>†</sup>Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF for **2**, **3** and **4**, atomic coordinates and displacement parameters, bond lengths, and bond angles; <sup>1</sup>H-<sup>1</sup>H COSY NMR; ESI mass spectra; diagrams of the selected Kohn–Sham molecular orbitals for the complexes and alkynyl ligands, contour project the deformation of electron density, energies and Mulliken composition of frontier KS molecular orbitals, and selected Wiberg bond indices. CCDC reference numbers 786915, 786916 and 805993. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11710j

phosphorescence quenching by molecular oxygen.<sup>11,20</sup> These complexes contain linear diphosphine ligands with spatially separated phosphorus atoms that determine the observed structural motif - a "core" of an emissive heterometallic cluster stabilized by an external gold(1)-phosphine "belt". As mentioned above, bridging diphosphines such as bis(diphenylphosphino)methane (dppm) are also capable of supporting the polynuclear aggregates, including the alkynyl ones.<sup>14,21</sup> Surprisingly, no alkynyl gold-containing compounds have been reported for the tridentate relative of dppm, tris(diphenylphosphino)methane (tppm), though a very few species (halide, dithiocarbamate) were characterized.<sup>22</sup> This prompted us to employ the tppm ligand toward the synthesis of luminescent coinage metal complexes, in particular, toward the preparation of Au(I) containing alkynyl clusters. Herein, we report on the assembly of a family of tetranuclear Au(I)-Cu(I) tppm-based clusters from the simple precursors, photophysical and theoretical investigations of the novel compounds.

## **Experimental**

#### **General comments**

Phenylacetylene (Acros); 1-ethynyl-4-methoxybenzene (Alfa Aesar); tetrahydrothiophene; tris(diphenylphosphino)methane (tppm) (Strem Chemicals) and all solvents were used as received. Triethylamine was distilled over KOH under a nitrogen atmosphere prior to use. [Au(tht)Cl] (tht = tetrahydrothiophene), $^{23}$  $[tppmAu_3Cl_3]^{24} [AuC_2C_6H_4CN]_n^{25} methyl-4-ethynylbenzo$ ate,<sup>26</sup> and 4-ethynylaniline<sup>27</sup> were synthesized according to published procedures. The solution  ${}^{1}H$ ,  ${}^{1}H-{}^{1}H$  COSY and  ${}^{31}P{}^{1}H$ NMR spectra were recorded on a Bruker-DX300 spectrometer. Mass spectra were determined on a Bruker micrOTOF 10223 instrument in the ESI<sup>+</sup> mode. Theoretical isotope patterns were calculated using the Sheffield ChemPuter program available free of charge on-line http://winter.group.shef.ac.uk/chemputer/. The IR and UV-Vis spectra were recorded using a Perkin Elmer FT-IR BX spectrometer and a Shimadzu UV 3600 spectrophotometer, respectively.

#### $[tppm(AuC_2C_6H_5)_3Cu]BF_4$ (1)

A solution of phenylacetylene (29.7 mg, 0.291 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml), and triethylamine (1 ml) were added dropwise to the suspension of [tppmAu<sub>3</sub>Cl<sub>3</sub>] (122.9 mg, 0.097 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) under vigorous stirring. A solution of [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> (30.6 mg, 0.097 mmol) in MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:1) was added slowly to the reaction mixture and the colorless suspension turned into a brilliant yellow solution. The reaction mixture was stirred for 2 h in the absence of light. The resulting transparent solution was reduced in volume in vacuo and diluted with hexane to give a bright yellow precipitate. The precipitate was filtered off, washed with hexane, and dried in vacuo. Yield: 129.3 mg (87%). IR (KBr, cm<sup>-1</sup>):  $v(C \equiv C)$  2086w. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>;  $\delta$ ): 42.1, s. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>;  $\delta$ ): phosphine: 6.38 (q, H-CP<sub>3</sub>, 1H, J<sub>PH</sub> 10.1 Hz), 7.14 (dd, H-meta Ph, 12H, J<sub>HH</sub> ca. 7 Hz), 7.23 (t, H-para Ph, 6H, J<sub>HH</sub> ca. 7 Hz), 7.96 (unresolved multiplet, H-ortho Ph, 12H), alkynyl ligands: 7.09 (dd, H-meta, 6H, J<sub>HH</sub> ca. 7 Hz), 7.28 (t, H-para, 3H, J<sub>HH</sub> ca. 7 Hz),

7.31 (d, H-*ortho*, 6H,  $J_{\rm HH}$  7.6 Hz). ESI (*m/z*): 1525 (MI<sup>+</sup>), calcd for Au<sub>3</sub>CuC<sub>61</sub>H<sub>46</sub>P<sub>3</sub>: 1525. Anal. calcd for C<sub>61</sub>H<sub>46</sub>Au<sub>3</sub>B<sub>1</sub>Cu<sub>1</sub>F<sub>4</sub>-P<sub>3</sub>: C, 45.42; H, 2.87. Found: C, 45.36; H, 3.03.

# [tppm(AuC<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COOMe)<sub>3</sub>Cu]BF<sub>4</sub> (2)

Triethylamine (1 ml) was added dropwise to a mixture of methyl-4-ethynylbenzoate (22.6 mg, 0.141 mmol), [tppmAu<sub>3</sub>-Cl<sub>3</sub>] (60.0 mg, 0.047 mmol) and [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> (14.8 mg, 0.047 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) under vigorous stirring. The reaction mixture was stirred for 2 h in the absence of light. The resulting transparent light-orange solution was reduced in volume in vacuo and diluted with hexane to give an orangeyellow precipitate. The precipitate was filtered off, washed with hexane and ether, and dried in vacuo. Yield: 81 mg (96%). IR (KBr, cm<sup>-1</sup>):  $v(C \equiv C)$  2113w,  $v(C \equiv O)$  1705s. <sup>31</sup>P{<sup>1</sup>H} NMR  $(CD_2Cl_2; \delta)$ : 41.7, s. <sup>1</sup>H NMR  $(CD_2Cl_2; \delta)$ : phosphine: 6.57 (q, H-CP<sub>3</sub>, 1H, J<sub>PH</sub> 10.2 Hz), 7.15 (dd, H-meta Ph, 12H, J<sub>HH</sub> ca. 7 Hz), 7.25 (t, H-para Ph, 6H, J<sub>HH</sub> ca. 7 Hz), 8.00 (unresolved multiplet, H-ortho Ph, 12H), alkynyl ligands: 3.92 (s, COOCH<sub>3</sub>, 9H), 7.44 (d, C<sub>6</sub>H<sub>4</sub>, 6H, J<sub>HH</sub> 8.2 Hz), 7.74 (d, C<sub>6</sub>H<sub>4</sub>, 6H,  $J_{\rm HH}$  8.2 Hz). ESI<sup>+</sup> (*m*/*z*): 1699 (MI<sup>+</sup>), calcd for Au<sub>3</sub>CuC<sub>67</sub>-H<sub>52</sub>P<sub>3</sub>O<sub>6</sub>: 1699. Anal. calcd for C<sub>67</sub>H<sub>52</sub>Au<sub>3</sub>B<sub>1</sub>Cu<sub>1</sub>F<sub>4</sub>O<sub>6</sub>P<sub>3</sub>: C, 45.02; H, 2.93. Found: C, 45.07; H, 3.02. Single crystals of 2 suitable for X-ray analysis were grown from CH<sub>2</sub>Cl<sub>2</sub> solution by Et<sub>2</sub>O slow diffusion at +5 °C.

#### [tppm(AuC<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN)<sub>3</sub>Cu]BF<sub>4</sub> (3)

Tppm (21.4 mg, 0.037 mmol) and [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> (11.8 mg, 0.037 mmol) were added dropwise to a suspension of  $[AuC_2C_{6-}]$ H<sub>4</sub>CN)]<sub>n</sub> (40.0 mg, 0.113 mmol), in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) under vigorous stirring. The reaction mixture was stirred for 3 h in the absence of light. The resulting transparent yellow solution was reduced in volume in vacuo and diluted with hexane, forming a vellow precipitate. The precipitate was filtered off, washed with hexane and ether, and dried in vacuo. Yield: 50 mg (80%). IR (KBr, cm<sup>-1</sup>):  $v(C \equiv C)$  2114w,  $v(C \equiv N)$  2226m. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>; δ): 41.5, s. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>; δ): phosphine: 6.44 (q, H-CP<sub>3</sub>, 1H, J<sub>PH</sub> 10.1 Hz), 7.16 (dd, H-meta Ph rings, 12H, J<sub>HH</sub> ca. 7 Hz), 7.26 (t, H-para Ph rings, 6H, J<sub>HH</sub> ca. 7 Hz), 7.94 (unresolved multiplet, H-ortho Ph rings, 12H), alkynyl ligands: 7.47 (s, C<sub>6</sub>H<sub>4</sub>, 12H). ESI (m/z): 1600 (MI<sup>+</sup>), calcd for the Au<sub>3</sub>-CuC<sub>64</sub>H<sub>43</sub>P<sub>3</sub>N<sub>3</sub>: 1600. Single crystals of **3** suitable for X-ray analysis were grown from CH<sub>2</sub>Cl<sub>2</sub> solution by Et<sub>2</sub>O slow diffusion at +5 °C.

### [tppm(AuC<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe)<sub>3</sub>Cu]BF<sub>4</sub> (4)

Triethylamine (1 ml) was added dropwise to a mixture of 1ethynyl-4-methoxybenzene (18.6 mg, 0.141 mmol), [tppmAu<sub>3</sub>-Cl<sub>3</sub>] (60.0 mg, 0.047 mmol), and [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> (14.8 mg, 0.047 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) under vigorous stirring. The reaction mixture was stirred for 1 h in the absence of light. The resulting transparent yellow solution was reduced in volume *in vacuo* and diluted with hexane, a yellow precipitate formed. The precipitate was filtered off, washed with hexane, and dried *in vacuo*. Yield: 52.9 mg (66%). IR (KBr, cm<sup>-1</sup>): v(C=C) 2069w.<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>;  $\delta$ ): 41.5, s. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>;  $\delta$ ): **phosphine**: 6.47 (q, <u>H</u>-CP<sub>3</sub>, 1H, *J*<sub>PH</sub> 9.9 Hz), 7.14 (dd, H*meta* Ph rings, 12H, *J*<sub>HH</sub> *ca*. 7 Hz), 7.22 (t, H-*para* Ph rings, 6H, *J*<sub>HH</sub> *ca*. 7 Hz), 7.99 (m, H-*ortho* Ph rings, 12H), **alkynyl ligands**: 3.81 (s, OCH<sub>3</sub>, 9H), 6.64 (d, C<sub>6</sub><u>H</u><sub>4</sub>, 6H, *J*<sub>HH</sub> 8.6 Hz), 7.27 (d, C<sub>6</sub><u>H</u><sub>4</sub>, 6H, *J*<sub>HH</sub> 8.6 Hz). ESI (*m*/*z*): 1615 (MI<sup>+</sup>), calcd for Au<sub>3</sub>CuC<sub>64</sub>H<sub>52</sub>P<sub>3</sub>O<sub>3</sub>: 1615. Anal. calcd for C<sub>64</sub>H<sub>52</sub>Au<sub>3</sub>B<sub>1</sub>Cu<sub>1</sub>-F<sub>4</sub>O<sub>3</sub>P<sub>3</sub>: C, 45.13; H, 3.08. Found: C, 45.05; H, 3.09. Single crystals of **4** suitable for X-ray analysis were grown from CH<sub>2</sub>Cl<sub>2</sub> solution by slow evaporation at +5 °C.

#### [tppm(AuC<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>3</sub>Cu]BF<sub>4</sub> (5)

Triethylamine (1 ml) was added dropwise to a mixture of 4-ethynylaniline (16.5 mg, 0.141 mmol), [tppmAu<sub>3</sub>Cl<sub>3</sub>] (60.0 mg, 0.047 mmol), and [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> (14.8 mg, 0.047 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) under vigorous stirring. The reaction mixture was stirred for 2 h in the absence of light and resulted in orange precipitate formation. All volatile components were removed *in vacuo* and the crystalline deposit washed with hexane, and dried *in vacuo*. Yield: 69.5 mg (89%). IR (KBr, cm<sup>-1</sup>):  $v(C\equiv C)$ 2063w.<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>;  $\delta$ ): 41.2, s. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO;  $\delta$ ): **phosphine**: 6.80 (q, H–CP<sub>3</sub>, 1H, *J*<sub>PH</sub> 10.0 Hz), 7.28 (dd, H-*meta* Ph rings, 12H, *J*<sub>HH</sub> *ca*. 7 Hz), 7.16 (t, H-*para* Ph rings, 6H, *J*<sub>HH</sub> *ca*. 7 Hz), 7.91 (unresolved multiplet, H-*ortho* Ph rings, 12H), **alkynyl ligands**: 5.58 (s br, NH<sub>2</sub>, 6H), 6.35

Table 1Crystallographic data for  $2-4^a$ 

(d,  $C_6H_4$ , 6H,  $J_{HH}$  8.2 Hz), 7.00 (d,  $C_6H_4$ , 6H,  $J_{HH}$  8.2 Hz). ESI (*m*/*z*): 1570 (MI<sup>+</sup>), calcd for Au<sub>3</sub>CuC<sub>61</sub>H<sub>49</sub>P<sub>3</sub>N<sub>3</sub>: 1570.

#### X-ray crystal structure determination

For single crystal X-ray diffraction experiments, crystals of **2**, **3** and **4** were fixed on micro mounts and placed on a Bruker Smart Apex II diffractometer and measured at temperature 210, 150 and 170 K, respectively, using monochromated MoK $\alpha$  radiation. Absorbance correction was applied according to the shape of crystals. The structures have been solved by direct methods using SHELX-97 program.<sup>28</sup> Positions of H atoms were modeled using a 'riding' model. Crystallographic data for **2–4** are collected in Table 1. Atomic coordinates and displacement parameters are presented in Tables S1–S4 (S denotes Supporting Information†) for **2**, **3** and **4**, respectively. Supplementary crystallographic data for this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC 786915, 786916 and 805993) and can be obtained free of charge *via* www.ccdc. cam.ac.uk/data\_request/cif.

#### **Photophysical measurements**

All photophysical measurements were carried out in  $CH_2Cl_2$ , which was distilled immediately prior to use. All solutions were carefully degassed before lifetime and quantum yield measurements. The light-emitting diode (LED, maximum emission at

| Compound  | 2   | 3   | 4   |
|---|---|---|---|
| Formula   | Au <sub>3</sub> BCuC <sub>67</sub> H <sub>52</sub> F <sub>4</sub> P <sub>3</sub> O <sub>6</sub> | Au <sub>3</sub> BCuC <sub>64</sub> H <sub>43</sub> F <sub>4</sub> P <sub>3</sub> N <sub>3</sub> | Au <sub>3</sub> BCuC <sub>64</sub> H <sub>52</sub> F <sub>4</sub> P <sub>3</sub> O <sub>3</sub> |
| Crystal System  | Trigonal  | Trigonal  | Trigonal  |
| a/Å   | 17.1354(7)  | 16.9942(7)  | 17.1541(8)  |
| b/Å   | 17.1354(7)  | 16.9942(7)  | 17.1541(8)  |
| c/Å   | 17.8646(8)  | 16.6654(11)   | 16.7640(8)  |
| $\alpha$ (°)  | 90  | 90  | 90  |
| $\beta$ (°)   | 90  | 90  | 90  |
| $\gamma$ (°)  | 120   | 120   | 120   |
| $V/Å^3$   | 4542.7(3)   | 4168.2(4)   | 4272.1(3)   |
| Molecular weight  | 1787.25   | 1688.17   | 1703.22   |
| Space group   | R3  | R3  | R3  |
| $\mu/\text{mm}^{-1}$  | 7.735   | 8.417   | 8.215   |
| T/K   | 210(2)  | 150(2)  | 170(2)  |
| Ζ   | 3   | 3   | 3   |
| $D_c/\mathrm{g}~\mathrm{cm}^{-3}$   | 1.960   | 2.018   | 1.986   |
| Crystal size/mm   | 0.1 	imes 0.1 	imes 0.1   | $0.35 \times 0.15 \times 0.10$  | 0.3 	imes 0.2 	imes 0.2   |
| Radiation   | Μο-Κα   | Μο-Κα   | Μο-Κα   |
| Total reflections   | 19 554  | 18 620  | 18 951  |
| Unique reflections  | 5889  | 5424  | 5509  |
| Angle range $2\theta/^{\circ}$  | 3.56-59.98  | 3.70-59.98  | 3.66-60.00  |
| Reflections with $ F_0  \ge 4\sigma_F$  | 4008  | 4868  | 4536  |
| R <sub>int</sub>  | 0.0405  | 0.0355  | 0.0306  |
| R <sub>o</sub>  | 0.0596  | 0.0423  | 0.0366  |
| $R_1 ( F_0  \ge 4\sigma_F)$   | 0.0273  | 0.0231  | 0.0217  |
| $wR_2 ( F_0  \ge 4\sigma_F)$  | 0.0436  | 0.0416  | 0.0395  |
| $R_1$ (all data)  | 0.0515  | 0.0292  | 0.0319  |
| $wR_2$ (all data)   | 0.0469  | 0.0427  | 0.0412  |
| Flack parameter   | -0.022(5)   | -0.019(5)   | 0.000(4)  |
| S   | 0.791   | 0.900   | 0.857   |
| $ ho_{ m min}, ho_{ m max},e/{ m \AA}^3$  | -0.607, 1.075   | -0.598, 1.285   | -0.527, 0.900   |
| ${}^{a}R_{1} = \Sigma   F_{1}  -  F_{2}   / \Sigma  F_{2}  \cdot wR_{2} = \{\Sigma$ | $\sum [w(F_{2}^{2} - F_{2}^{2})^{2}] / \sum [w(F_{2}^{2})^{2}] \}^{1/2}$ ; $w = 1/[\sigma$      | ${}^{2}(F_{2}^{2})+(aP)^{2}+bP$ , where $P=(F_{2}^{2}+2F_{2})$                                  | $(x^2)/3: s = {\Sigma[w(F_s^2 - F_s^2)]/(n - f_s^2)]}/{n}$                                      |

 ${}^{a}R_{1} = \Sigma ||F_{0}| - |F_{c}|| \Sigma |F_{0}|; wR_{2} = \{\Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}] \Sigma [w(F_{0}^{2})^{2}] \}^{1/2}; w = 1/[\sigma^{2}(F_{0}^{2}) + (aP)^{2} + bP], where P = (F_{0}^{2} + 2F_{c}^{2})/3; s = \{\Sigma [w(F_{0}^{2} - F_{c}^{2})]/(n - p)\}^{1/2} where n is the number of reflections and p is the number of refinement parameters.$ 

385 nm) was used to pump luminescence. The LED was used in the continue and pulse modes (pulse width, 1–20 µs; duty of edge ~90 ns; repetition rate, 100 Hz to 10 kHz). A digital oscilloscope Tektronix TDS3014B (Tektronix, bandwidth 100 MHz), monochromator MUM (LOMO, interval of wavelengths 10 nm) and photomultiplier tube Hamamatsu were used for lifetime measurements. Emission spectra were recorded using an HR2000 spectrometer (Ocean Optics). A halogen lamp, LS-1-CAL (Ocean Optics), and deuterium lamp, DH2000 (Ocean Optics), were used to calibrate the absolute spectral response of the spectral system in the 200–1100 nm range. The absolute emission quantum yield was determined by Vavilov's method using LED pumping and rhodamine 6G in ethanol ( $\Phi_{em} = 0.95 \pm 0.03$ ) as standard with the refraction coefficients of dichloromethane and ethanol equal to 1.42 and 1.36, respectively.<sup>29</sup>

#### Computational details for DFT and TD-DFT calculations

Compounds 3 and 5 with different X substituents in the alkynyl ligands were chosen to investigate and to assign the effects of the X on the spectral and photophysical properties. The influence of the Cu(1) ion incorporated in the central  $\{AuC_2C_6H_4X\}_3$  cluster on the spectral behavior of these complexes was studied by comparison of 3 with the model system [tppm(AuC\_2C\_6H\_4CN)\_3], 3a, which does not contain the hetero ion. Geometry optimizations were performed on 3, 3a, and 5 in the absence of solvent using the hybrid exchange–correlation functional PBE0 (also known as PBE1PBE) in combination with the SDD+DZVP basis set.<sup>30</sup> The SDD basis set with relativistic effective core potentials was used for the heavy metal atoms and the all-electron DZVP basis set for hydrogen, carbon, nitrogen, and oxygen atoms.<sup>31</sup>

Frequency analysis has shown that the optimized structures correspond to the energy minima on the potential surface. All TD-DFT calculations for the singlet and triplet excited states were carried out using these optimized ground-state geometries. The geometry of the lowest-energy triplet state of **3** and **5** was also optimized using an unrestricted formalism (SCF approach). The results of the calculations are summarized in Table 4.

The DFT calculations were carried out using the Gaussian 03 package.<sup>32</sup> ChemCraft program was employed for 3D visualization of Kohn–Sham orbitals. The contour maps of the electron density deformation were plotted by the Chemissian program http://www.chemissian.com. Notation of the low lying electronic states is shown in Scheme 1 (the geometry used in the calculations is indicated in brackets).



#### Scheme 1

#### **Results and discussion**

#### Synthesis and characterization

The reactions of the trinuclear gold complex [tppmAu<sub>3</sub>Cl<sub>3</sub>] with a stoichiometric amount of  $HC_2C_6H_4X$  (X = H, COOMe, CN, OMe, NH<sub>2</sub>) and Cu<sup>+</sup> in the presence of a deprotonating agent (NEt<sub>3</sub>) resulted in formation of the novel heterometallic [tppm (AuC<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X)<sub>3</sub>Cu]<sup>+</sup> complexes **1–5** in good yields (see Scheme 2), which were isolated as  $BF_4^-$  salts after recrystallization.

The moderately air-stable yellow to orange complexes 1–5 were characterized by <sup>1</sup>H, <sup>1</sup>H–<sup>1</sup>H COSY, <sup>31</sup>P{<sup>1</sup>H} NMR and ESI-MS spectroscopy. The structures of 2–4 in the solid state were determined by X-ray diffraction analysis. The molecular views of 2–4 cations together with essential structural parameters are given in Fig. 1; crystallographic data are summarized in Table 1.

Compounds **2–4** are isostructural and contain the { $(AuC_2C_6-H_4X)_3Cu$ } skeleton stabilized by coordination to the tridentate phosphine. Three {PAuC\_2C\_6H\_4X} "rods" held together by the phosphine, Cu–Au, Cu– $\pi$ -C=C, and Au–Au bonding are slightly twisted to form a distorted tetrahedral {Au<sub>3</sub>Cu}. The symmetry of these complexes involves a threefold axis passing through the Cu(1)–C(1)–H(1) as well as F(1)–B(1) atoms of the BF<sub>4</sub><sup>-</sup> anion. The Au–P distances in **2–4** are nearly identical (2.282(1)–2.285(1) Å) and fit well with the values previously reported for Au–P bond lengths.<sup>22,24,33</sup> The Au–Au contacts from 3.1843(4) to 3.2388(3) Å fall in the range typical for aurophilic interactions in the "Au<sub>3</sub>" clusters supported by the tridentate phosphine, <sup>17,18,22,24,33,34</sup> "Au<sub>4</sub>" alkynyl–phosphine cluster,<sup>35</sup> and slightly shorter than Au–Au distances found in the other alkynyl and alkynyl-phosphine Au(1)–Cu(1) compounds.<sup>15,36–39</sup>

The Cu–Au contacts were found to be 2.9565(9), 2.9538(7) and 2.9278(7) Å for **2**, **3** and **4**, respectively, which are essentially lower than the sum of the Au and Cu van der Waals radii (3.06 Å). Due to geometrical constraints the  $\pi$ -C=C–Cu interaction is asymmetric, the Cu–C distances for a certain triple bond differ substantially, see caption to Fig. 1. The C=C bond lengths in **2**, **3** and **4** are significantly shorter than those found earlier in stable clusters containing effective alkynyl–copper bonds <sup>9,15,20,37,40,41</sup> that evidently implies rather weak  $\pi$ -bonding of the alkynyl ligands to the copper ion.

In the crystal cell the cluster cations are "head-to-tail" packed to form infinite columns (see Fig. 2 and Fig. S1<sup>†</sup>), where the



Scheme 2 Synthesis of the complexes 1-5.



Fig. 1 Molecular views of the cations 2, 3 and 4. Selected interatomic distances (Å) for 2 are P(1)-Au(1) = 2.2816(13), Au(1)-Au(1) = 3.2388(3), Au(1)-Cu(1) = 2.9565(9), Au(1)-C(2) = 2.007(6), Cu(1)-C(2) = 2.138(5), Cu(1)-C(3) = 2.357(5), C(2)-C(3) = 1.220(7); for 3 are P(1)-Au(1) = 2.2851(11), Au(1)-Au(1) = 3.1843(3), Au(1)-Cu(1) = 2.9538(7), Au(1)-C(2) = 2.016(5), Cu(1)-C(2) = 2.123(4), Cu(1)-C(3) = 2.376(4), C(2)-C(3) = 1.207(6); for 4 are P(1)-Au(1) = 2.2828(10), Au(1)-Au(1) = 3.1937(3), Au(1)-Cu(1) = 2.9278(7), Au(1)-C(2) = 2.018(5), Cu(1)-C(2) = 2.130(4), Cu(1)-C(3) = 2.453(4), C(2)-C(3) = 1.204(6).



Fig. 2 View of the infinite column structure formed in the crystalline phase of 3.

constituting units are bound to each other through hydrogen bonds, which involve the  $\mathrm{BF}_4$  anions.

Complexes 1 and 5 didn't give single crystals suitable for Xray analysis and their structures have been established on the basis of spectroscopic data. The ESI mass spectra of the compounds studied (Figs. S2-S6<sup>†</sup>) display signals of the singly charged  $[tppm(AuC_2C_6H_4X)_3Cu]^+$  molecular ions, the m/zvalues and isotopic patterns of which completely match the calculated ones. The  ${}^{31}P{}^{1}H$  NMR spectra of 1-5 display singlet resonances at ca. 41 ppm that corresponds to all equivalent phosphorus atoms of the triphosphine ligand and is compatible with the presence of the threefold axis in the molecules under study. The number of signals in the <sup>1</sup>H NMR spectra of 1-5 and their relative intensities fit well the structural patterns shown in Scheme 2, as well as the solid state structures revealed for 2-4. Assignment of the signals observed in the <sup>1</sup>H NMR spectra of 1, 4, and 5 was additionally supported by <sup>1</sup>H<sup>-1</sup>H COSY spectra because the aromatic resonances were not clearly resolved in 1D <sup>1</sup>H NMR. The high-field quartet at 6.5 ppm ( $J_{\rm PH}$  ca. 10 Hz, 1H) corresponds to the CH group of tppm. Two clearly resolved doublets (6H per signal) in the 6.35–7.74 ppm range arise from the ortho- and meta-protons of the alkynyl phenylene spacer, excluding 3 where these two doublets overlap to give a singlet with 12H integral intensity. The strong-field singlets at 3.92, 3.81 and 5.58 ppm for 2 (9H), 4 (9H) and 5 (6H), respectively, correspond to the protons of the X substituent. The low-field multiplets (7.14-8.00 ppm, see Experimental), which display correlations in the corresponding COSY spectra, Figs. S7-S9<sup>†</sup>, are evidently generated by the protons of the phosphine phenyl rings. It is worth noting that the chemical shifts of these signals are nearly identical for all clusters studied. This observation together with the relative intensity and multiplicity of the signals clearly supports the suggested assignment. The solid-state IR spectra of 1–5 expectedly show a low frequency shift of  $C \equiv C$ stretching bands (in the range from 2063 to 2226  $\text{cm}^{-1}$ ) as a result of coordination of the C=C triple bonds to the metal ions. These spectroscopic data obtained show that the general structural motif found in the solid state remains unchanged in solution.

**Table 2** Photophysical properties of the complexes 1–5 in  $CH_2Cl_2$  solution, 25 °C,  $\lambda_{ex} = 385$  nm

|   |                       |   |                       |                         |               |             |                        |               |                              | <i>.</i> .                    |                                |         |
|---|-----------------------|---|-----------------------|-------------------------|---------------|-------------|------------------------|---------------|------------------------------|-------------------------------|--------------------------------|---------|
|   | Uammatt               | 1 nm  | 2 b                   | 2                       | Q.Y., %       |             | $\tau_{\rm obs},\mu s$ |               | $k_{\text{nonrad}}, 10^{-1}$ | <sup>-6</sup> s <sup>-1</sup> | $k_{\rm rad}, 10^{-6} {\rm s}$ | -1      |
|   | constant <sup>a</sup> | $(\varepsilon \times 10^{-3},  \mathrm{cm}^{-1} \mathrm{M}^{-1})$ | nm                    | λ <sub>em</sub> ,<br>nm | Degassed      | Aerated     | Degassed               | Aerated       | Degassed                     | Aerated                       | Degassed                       | Aerated |
| 1 | 0                     | 270sh (32); 319sh (12);<br>390 (1)                                | 270; 309;<br>390      | 560                     | $1.7\pm0.2$   | $1.4\pm0.2$ | $2.8\pm0.1$            | $1.45\pm0.08$ | 0.35                         | 0.68                          | 0.006                          | 0.009   |
| 2 | 0.45                  | 256 (101); 268sh (92);<br>300sh (42); 341 (18);<br>387 (3)        | 293; 345;<br>387w     | 560                     | $4.0\pm0.6$   | $1.0\pm0.2$ | $7.0\pm0.4$            | $2.8\pm0.1$   | 0.14                         | 0.35                          | 0.006                          | 0.004   |
| 3 | 0.66                  | 290 (56); 305 (54);<br>326sh (38);<br>390 (5); 484 (1)            | 270; 305;<br>390      | 550                     | $5.2\pm0.8$   | $3.1\pm0.5$ | $6.8\pm0.4$            | $2.8\pm0.1$   | 0.14                         | 0.35                          | 0.008                          | 0.011   |
| 4 | -0.27                 | 258 (95); 287sh (58);<br>342 (16); 404 (3)                        | 270; 302;<br>339; 396 | 580                     | $1.9\pm0.3$   | $1.2\pm0.2$ | $0.95\pm0.05$          | $0.63\pm0.04$ | 1.0                          | 1.6                           | 0.02                           | 0.02    |
| 5 | -0.66                 | 271 (26); 314sh (16);<br>338 (13); 357sh (11);<br>424w (3)        | 309; 342;<br>365; 424 | 680                     | $0.6 \pm 0.1$ | $0.4\pm0.1$ | $0.44\pm0.02$          | $0.30\pm0.02$ | 2.2                          | 3.3                           | 0.02                           | 0.01    |

<sup>a</sup> Hammett constants of the X substituent.<sup>43 b</sup> The maximum of bands in the excitation spectra.



Fig. 3 The UV-Vis absorption and emission spectra of 1–5.

#### **Photophysical properties**

The photophysical and spectroscopic data for complexes 1–5 are summarized in Table 2, the UV-Vis absorption and emission spectra in dichloromethane are shown in Fig. 3. The absorption spectra of the compounds are essentially similar. The broad higher-energy absorptions below 290 nm can be ascribed to the intra-ligand  $\pi \rightarrow \pi^*$  transitions of the alkynyl {C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X} moieties and phosphine ligand rings. This assignment is consistent with the previous reports on the related alkynyl–phosphine complexes, for which the prevalent absorption in the spectral range 250–300 nm, in general, is ascribed to the characteristic bands of the alkynyl and phosphine ligands.<sup>11,15,38,42</sup> As for the lower energy absorption bands, the TD-DFT calculations have been used to interpret these electronic transitions, *vide infra*.

All compounds studied exhibit room temperature luminescence in solution (Fig. 3, Table 2). Variation of the *para*-substituents in the alkynyl groups from the electron-withdrawing CN to the electron-donating  $NH_2$  allowed for the monitoring of the ligands' electronic effect onto the photophysical characteristics of these complexes. Emission band maxima fall in 550–680 nm range and display a systematic red shift with the increase in **X** substituent donicity together with the related decrease of



Fig. 4 The correlations between Hammett constants of the X substituent and emission wavelength, luminescence lifetime, and quantum yield for 1–5;  $\blacksquare$  emission band maxima;  $\blacklozenge$  quantum yield;  $\bigvee$  lifetime.

luminescence lifetime and quantum yield, Fig. 4. A similar trend was observed earlier for the Au(1)–Cu(1) "rods-in-belt" clusters,<sup>41</sup> where variations of luminescence wavelength were rationally ascribed to the changes in the energy of ground state orbitals involved in the emission. Similar to related heterometallic gold–copper alkynyl phosphine complexes<sup>11,15,37–39,42</sup> the excited state lifetimes for **1–5** fall in the microsecond domain that point to the triplet origin of the emission. It is worth mentioning that emission quantum yield and lifetime for all the complexes show nearly no luminescence quenching by molecular oxygen, which is an indication of effective shielding of the chromophoric center by external ligand environment.

#### **Computational studies**

Structural and electronic properties of the complexes under study were elucidated by density functional calculations (see the Experimental for notation and computational details). Selected calculated structural parameters of the ground and excited triplet states for **3**, **5** and the model compound **3a** (without Cu(I) ion)

|                  |        | 3                |                  | :                | 3a               |                  |
|------------------|--------|------------------|------------------|------------------|------------------|------------------|
|                  | Exper. | Calc. $S_0(S_0)$ | Calc. $T_1(T_1)$ | Calc. $S_0(S_0)$ | Calc. $T_1(T_1)$ | Calc. $S_0(S_0)$ |
| Cu–Au            | 2.954  | 2.982            | 2.971            | 2.955            | 2.964            |                  |
| Au–Au            | 3.184  | 3.264            | 3.263            | 3.292            | 3.161            | 3.364            |
| Au–P             | 2.285  | 2.334            | 2.335            | 2.328            | 2.326            | 2.327            |
| Au-C(2)          | 2.016  | 2.010            | 2.000            | 2.006            | 2.005            | 1.986            |
| Cu-C(2)          | 2.123  | 2.129            | 2.130            | 2.137            | 2.109            |                  |
| Cu-C(3)          | 2.376  | 2.456            | 2.203            | 2.434            | 2.301            |                  |
| C=C              | 1.207  | 1.234            | 1.232            | 1.237            | 1.251            | 1.226            |
| Cu-C(1)          | 5.183  | 5.188            | 5.379            | 5.135            | 5.245            |                  |
| Au - C(2) - C(3) | 175.0  | 176.4            | 171.7            | 176.9            | 173.0            | 175.5            |

**Table 3** Selected interatomic distances (Å) and Au–C(2)–C(3) angles (deg) for 3, 5, and 3a

are given in Table 3. All of the studied complexes retain the structural motif (Fig. 1 and Scheme 2) during the geometry optimization, and the changes in structural parameters are fairly small. However, it is worth noting that the calculated Au-Au, Au-C, and Au-P distances are markedly longer than those found in the solid state structures. It was also found that in 3 and 5 the bond order indices are quite similar for the atoms related to the {Au<sub>3</sub>Cu} cluster core (see Table S8<sup>†</sup>). The observed appreciable Stokes shifts are indicative of distinguishable structural changes associated with the intersystem crossing and formation of the emissive triplet state. In the T<sub>1</sub> excited state a decrease in the Au–C $\equiv$ C angles results in a shortening of the Cu–C(2) distances in the triplet excited states as compared to the ground states (Table 3). In addition, in the  $T_1$  state the Wiberg indices of the Cu-(C=C) bonds increase, and the indices of the C=C bonds decrease.<sup>44</sup> These changes are caused by the distortion of the geometry of these complexes.

As the symmetry of the {Au<sub>3</sub>Cu} metal core is close to  $C_{3y}$ many Kohn-Sham (KS) orbitals including the frontier ones are pseudo-degenerated, and the orbitals shown in Fig. 5 are distorted due to the mixing of two components. The energies of the frontier KS molecular orbitals of 3 and 5 are essentially different, which evidently reflects the effect of the alkynyl ligand substituents:

|       | HC    | MO    | LUMO  |       |  |
|-------|-------|-------|-------|-------|--|
|       | 3     | 5     | 3     | 5     |  |
| ε, eV | -8.44 | -7.06 | -4.64 | -3.97 |  |

For compounds 3 and 5, the HOMO's are mainly located at the alkynyl  $\{C_2C_6H_4X\}$  moieties and the Cu(I) center. In the model complex 3a the HOMO orbital is mostly centered at the alkynyl ligand with a small contribution from the gold centers. The LUMO's of 3, 5 and 3a are mainly located on the tppm ligand with some admixture of the Au(I) atomic orbitals.

The major contribution into the two lowest almost degenerated singlet-singlet transitions is related to the HOMO→LUMO excitation. Thus, the absorption in the 300-360 nm range (complexes 3, 5) can be assigned to the electronic transitions from the  $[{Cu}, {C_2C_6H_4}]$  fragments to the  $\{Au_3\}$  skeleton and empty antibonding orbitals of the phosphine ligand. On the contrary, the low energy transitions in the model complex 3a correspond to the inter-ligand transfer  $\{C_6H_4\} \rightarrow \{PPh_2\}$ , that is indicative of a significant influence of the copper center on the spectral



Fig. 5 Frontier KS molecular orbitals of 3, 5 and 3a (top = LUMO, bottom = HOMO),  $\pm 0.03$  isosurface value.

behavior of the heterometallic complexes. It was also found that the energy and the composition of the HOMOs depend on the nature of the X substituent. The contribution of the alkynyl -C<sub>6</sub>H<sub>4</sub>- fragment to the HOMO in 5 (with the donor X) is appreciably higher than in 3 (with acceptor X) while the percentage of Cu(1) orbitals is higher in 3 compared to 5 (see Figs. S10-13 and Table S7<sup>†</sup>). Thus, the replacement of the CN substituent for NH<sub>2</sub> results in a reduction of the HOMO/LUMO gap due to a larger increment of the HOMO energy in comparison to that of the LUMO. This observation is completely in line with the observed variations of luminescence parameters of the complexes under study where the increase in electron-donor ability of the X group shifts the emission energy to lower values.

Only the lowest spin-forbidden transition was modeled, since phosphorescence usually occurs from the lowest triplet  $(T_1)$ excited state. For 5 the calculated energy of  $T_1$  is lower than that for **3** as well as the energy of  $S_1$  and the HOMO/LUMO gap. However, the results of the TD-DFT calculations give markedly overestimated values of the emission energies for both complexes (Table 4). Additionally, the TD-DFT approach didn't reveal a dominant configuration of the triplet state for 3, therefore the description of this state on the basis of the ground state

**Table 4** DFT energies (eV) of the lowest singlet and triplet states of 3and 5 and the HOMO/LUMO gap (for notation see Scheme 1)

|                                    | 3    | 5    |
|------------------------------------|------|------|
| HOMO/LUMO gap, $S_0(S_0)$          | 3.80 | 3.09 |
| $S_0(S_0)$                         | 0.00 | 0.00 |
| $S_0(T_1)$                         | 0.39 | 0.34 |
| $S_1(S_0)$ TD-DFT                  | 2.93 | 2.47 |
| $T_1(S_0) \xrightarrow{\text{RE}}$ | 2.81 | 2.39 |
| $T_1(S_0)$ TD-DFT                  | 2.62 | 2.28 |
| $T_1(T_1)$                         | 2.26 | 2.09 |
| $T_1(T_1) - S_0(T_1)$              | 1.87 | 1.76 |
| $E_{\rm em}({\rm exper.})$         | 2.25 | 1.82 |



**Fig. 6** Isosurfaces of the natural orbitals based on the electron density difference  $(S_0-T_1)$  for the complexes **3** with optimized  $S_0$  geometry: the orbital, from which the electron is excited (left), and the orbital, to which the electron is transferred (right).

frontier orbital analysis should be done with caution. Presumably, it is more appropriate to draw conclusions on the electronic structure of the lowest triplet from the orbitals of the optimized excited state (SCF scheme). Within the framework of the SCF approach the emission energies were estimated as  $E_{\rm em}$  =  $E(T_1(T_1)) - E(S_0(T_1))$  to take into account the geometrical relaxation of the emitting  $T_1$  state and the distortion of geometry from  $S_0(S_0)$  to  $S_0(T_1)$ . In general, the emission energy obtained by this method is underestimated compared to the experimental data, especially for complex 3. According to these results the major contribution to the  $T_1 \rightarrow S_0$  transition is made by the electronic density redistribution inside the {(C=C-Au)<sub>3</sub>Cu} core fragment; this type of emissive transition can be described as "intracore" charge transfer, see Fig. 6 and S14<sup>+</sup>. It is worth noting that the copper ion in the complexes under study determines the nature and properties of the lowest triplet electronic structure. For the complexes 1–5 the intra-ligand  $\pi$ - $\pi$  and charge transfer transitions are also responsible for the observed emission.

# Conclusions

In summary, a new family of tetranuclear Au(1)–Cu(1) alkynyl clusters supported by a tridentate phosphine ligand (tppm) has been synthesized using a self-assembly reaction of simple precursors under basic conditions. The complexes [tppm(AuC<sub>2</sub>C<sub>6</sub>-H<sub>4</sub>**X**)<sub>3</sub>Cu]<sup>+</sup> (**X** = H, COOMe, CN, OMe, NH<sub>2</sub>) display a general structural motif which contains heteronuclear {Au<sub>3</sub>Cu} cluster

core, stabilized by tripodal phosphine ligand and alkynyl groups. All the compounds studied exhibit phosphorescence in solution at room temperature with emission maxima in the range 550–680 nm. Luminescence properties of these clusters depend on the electron donor properties of the aromatic alkynyl ligands, which were varied *via* changing the **X** substituents in the *para* positions of the -C<sub>6</sub>H<sub>4</sub>- groups; increase in basicity of **X** causes a bathochromic shift of the emission maxima. The latter is clearly exemplified by the correlation of emission parameters with the corresponding Hammett constants. Quantum chemical calculations provide a deeper insight into the structural, electronic and spectroscopic properties of this novel family of gold–copper alkynyl–phosphine complexes and show that the observed long-wavelength phosphorescence is associated with metal centered triplet emission within the heterometallic alkynyl cluster.

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