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Synthesis and Crystal Structure of a Luminescent One-dimensional Phenylacetylide–Gold(I) Polymer with 2,6-Bis(diphenylphosphino)pyridine as Ligand

Shen-Jye Shieh,^a Xiao Hong,^b Shie-Ming Peng^{*,a} and Chi-Ming Che^{*,a,b}^a Department of Chemistry, National Taiwan University, Taipei, Taiwan^b Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

The emissive one-dimensional gold(I) polymer $[\{Au_2L(C\equiv CPh)_2\}_\infty]$ [$L = 2,6$ -bis(diphenylphosphino)pyridine] has been prepared and its crystal structure determined; $Au_2L(C\equiv CPh)_2$ is the repeating unit and the closest intermolecular $Au^1 \cdots Au^1$ separation is $3.252(1)$ Å.

New organometallic polymers with intriguing electrooptical properties have been receiving our close attention. Recent studies by Puddephatt and co-workers¹ have shown a way to assemble linear-chain metal-containing polymers by reacting gold(I) acetylides with diphosphine and/or functional isocyanide ligands. However, the crystal structures of the gold(I) oligomers have not been determined. We therefore present herein the preparation and crystal structure of the one-dimensional gold(I) polymer $[\{Au_2L(C\equiv CPh)_2\}_\infty]$ [$L = 2,6$ -bis(diphenylphosphino)pyridine], which is strongly emissive at room temperature.

The ligand L (ref. 2) and $[\{Au(C\equiv CPh)\}_\infty]^3$ were prepared by literature methods. The reaction of L (0.14 g) with $[\{Au(C\equiv CPh)\}_\infty]$ (0.10 g) in CH_2Cl_2 (40 cm³) at room temperature for 30 min gave a yellow solution which was filtered. Upon diffusion of diethyl ether into the solution, bright yellow crystals of $[\{Au_2L(C\equiv CPh)_2\}_\infty]$ were obtained in ca. 60% yield. This is an air-stable compound but has very low solubility in most common organic solvents. Satisfactory C, H and N analyses were obtained and its structure established by X-ray crystallography. Fig. 1 shows a perspective view of the

molecule.[†] The structure features a one-dimensional polymer with the repeating unit $Au_2L(C\equiv CPh)_2$ held together by a weak

[†] Crystal data. $C_{45}H_{33}Au_2NP_2$, $M = 1043.63$, orthorhombic, space group $Fdd2$, $a = 10.754(3)$, $b = 40.453(10)$, $c = 17.218(8)$ Å, $U = 7491(4)$ Å³, $Z = 8$, $D_c = 1.851$ g cm⁻³, crystal dimensions $0.10 \times 0.25 \times 0.40$ mm, $\mu = 79.18$ cm⁻¹, $F(000) = 3983$, number of parameters 227, number of unique reflections 1698, number of reflections with $I > 2\sigma(I)$ 1559, $R[\Sigma|F_o - F_c|/|F_o|] = 0.027$, $R'[\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2} = 0.020$, goodness of fit $\{[\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{1/2}\} = 1.98$, weighting scheme $w = 1/\sigma^2(F_o)$. Raw intensities were collected on a Nonius CAD4 fully automated four-circle diffractometer (graphite-monochromatized Mo-K α radiation, $\lambda = 0.7107$ Å) using the ω - 2θ scan mode. Data reduction and structure refinement were performed using the NRCC-SDP-VAX packages available from S. M. Peng upon request. The absolute structure was checked. The structure was solved by the Patterson method and refined by least-squares analysis. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

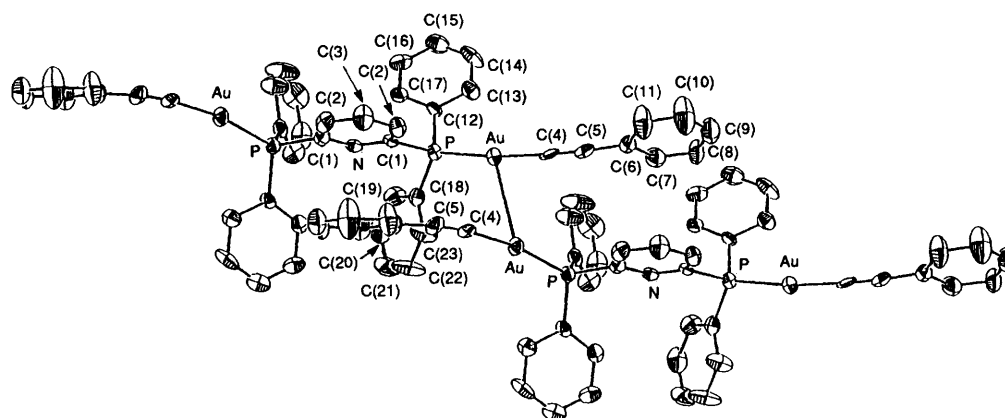


Fig. 1 A perspective view of $[\{Au_2L(C\equiv CPh)_2\}_\infty]$ showing the repeating $Au_2L(C\equiv CPh)_2$ unit held together by an $Au^1 \cdots Au^1$ interaction; $Au \cdots Au$ $3.252(1)$, $Au-P$ $2.270(3)$, $Au-C(4)$ $1.988(12)$, $C(4)-C(5)$ $1.199(17)$ Å; $Au-C(4)-C(5)$ $172.5(11)$, $P-Au-C(4)$ $170.5(3)$, $P-C(1)-N$ $117.7(11)^\circ$. Symmetry coordinates: (x, y, z) , $(-x, -y, -z)$, $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$, $(-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2})$

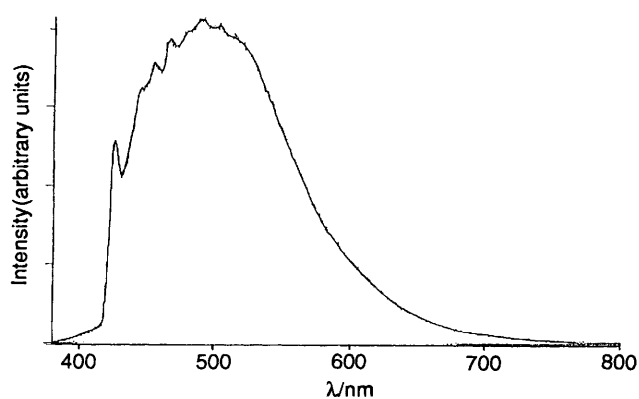


Fig. 2 Solid-state emission spectrum of $[\{Au_2L(C\equiv CPh)_2\}_\infty]$ measured at 77 K. Excitation at 350 nm

gold-gold interaction. For each $Au_2L(C\equiv CPh)_2$ unit, the two P and the N atoms of L and the two Au^I atoms are in a zigzag chain and a two-fold axis passes through the pyridine ring. The closest intermolecular $Au^I \cdots Au^I$ separation is 3.252(1) Å, which is slightly longer than the related value of 3.153(2) Å in $[Au_2(dppe)(C\equiv CPh)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane].⁴ This distance, however, falls in the normal range of ca. 2.75–3.40 Å for weak intermolecular interactions between Au^I centres.⁵ The $\nu(C\equiv CPh)$ absorption occurs at 2111 cm^{-1} , suggesting no intermolecular interaction between Au^I and the co-ordinated phenylacetylide.

The $[\{Au_2L(C\equiv CPh)_2\}_\infty]$ complex is a strongly emissive material in the solid state at room temperature. The emission (λ_{max} 500 nm) displayed in Fig. 2, is at a lower energy than the intraligand phosphorescence of the co-ordinated phenylacetyl-

ide (λ_{max} 400–450 nm)⁴ but is at a higher energy than the solid-state emission of $[Au_2(dppe)(C\equiv CPh)_2]$ (λ_{max} 550 nm).⁴ If the emission occurs from a $^3[d_\delta, p_\sigma^*]$ or $^3[d_\sigma, p_\sigma^*]$ excited state,^{4,6} then the difference in the solid-state emission energies between $[\{Au_2L(C\equiv CPh)_2\}_\infty]$ and $[Au_2(dppe)(C\equiv CPh)_2]$ could be rationalized by the longer intermolecular metal-metal separation in the former.

Acknowledgements

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