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The $^3(\pi\pi^*)$ Emission of $Cy_3PAu(C\equiv C)_nAuPCy_3$ ($n = 3, 4$). Effect of Chain Length upon Acetylenic $^3(\pi\pi^*)$ Emission

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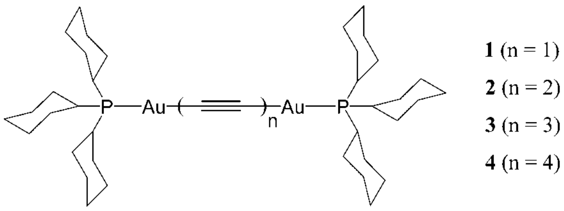
*Summary: The $Cy_3PAu(C\equiv C)_nAuPCy_3$ ($n = 3$ (**3**), 4 (**4**)) complexes were prepared by the reaction of $Me_3Si(C\equiv C)_nSiMe_3$ ($n = 3, 4$) with Cy_3PAuCl in the presence of NaOH. The molecular structure of **3**·CH_2Cl_2 was determined by X-ray crystallography. Complexes **3** and **4** show vibronically structured acetylenic $^3(\pi\pi^*)$ emission with ν_{0-0} values of 19 920 and 17 420 cm^{-1}, respectively; hence, ν_{0-0} for $Cy_3PAu(C\equiv C)_\infty AuPCy_3$ can be estimated at ~11 000 cm^{-1} from the plot of ν_{0-0} versus 1/n.*

While rigid, π-conjugated sp carbon chains have been incorporated as building blocks into myriads of electronic optics (molecular wires, NLOs),[1] spectroscopic investigations, especially regarding electronic transitions associated with $(C\equiv C)_n^{2-}$ chains, are sparse.[1g,2−7] Fundamental studies on the spectroscopic properties of oligoynes will facilitate the design of advanced optoelectronic materials; for example, the triplet emission from $(C\equiv C)_n^{2-}$ chains could be of great interest for OLED applications[8] and characterization of one-dimensional carbon allotrope, i.e., carbyne.[9] On the basis of the UV/vis spectra of monodispersed oligomers, Hirsch[7] and Gladysz[4a] estimated the limit of the lowest energy $^1(\pi\pi^*)$ absorption of $R(C\equiv C)_\infty R$ (R = CN, ^{t}Bu, Et_3Si, (η^5-C_5Me_5)Re(NO)(PPh_3)) to be λ_{max} 550 nm, *irrespective of end groups*. Our recent work[10] on luminescent $Cy_3PAu(C\equiv C)_nAuPCy_3$ ($n = 1$ (**1**), 2 (**2**)) (Chart 1) revealed that the lowest-energy acetylenic $^3(\pi\pi^*)$ excited states acquire sufficient allowedness via Au spin−orbit coupling to appear prominently in both electronic absorption and emission spectra. The λ_{0-0} lines for **1** and **2** are observed at 331 and 413 nm, respectively. The following questions naturally arise: what are the λ_{0-0} values of the acetylenic $^3(\pi\pi^*)$ excited states of the higher homologues, and is there a limit for the λ_{0-0} values? That is, how red can the triplet emission of $(C\equiv C)_n^{2-}$ chains be manipulated?

Chart 1



The two higher homologues, $Cy_3PAu(C\equiv C)_3AuPCy_3$ (**3**) and $Cy_3PAu(C\equiv C)_4AuPCy_3$ (**4**), have been synthesized. The reaction of $Me_3Si(C\equiv C)_3SiMe_3$ and $Me_3Si(C\equiv C)_4SiMe_3$ with Cy_3PAuCl in MeOH in the presence of NaOH gave the desired complexes as air-stable pale yellow plates and needles, respectively, after flash chromatography on alumina and recrystallization from CH_2Cl_2/Et_2O. These two complexes feature the unprecedented dinuclear gold(I) complexes bridged by C_6^{2-} and C_8^{2-} rods. Although the cyclohexyl groups of the phosphine ligands render improved solubility for these two complexes, they are still difficult to dissolve in common organic solvents, even CH_2Cl_2 and $CHCl_3$. We have been able to obtain dilute CH_2Cl_2 solutions of **3** and **4**, so that spectroscopic properties in fluid solutions can be explored.

Figure 1 shows the perspective view of **3**·CH_2Cl_2, which has a dumbbell shape with the crystallographic rotation center located at the center of the hexatriynediyl unit. The two-coordinate Au atoms are bridged by a virtually linear C_6^{2-} chain with P(1)−Au(1)−C(1), Au(1)−C(1)−C(2), C(1)−C(2)−C(3), and C(2)−C(3)−C(3*) angles of 174.1(2), 172.6(8), 176.7(9), and 179.4(14)°, respectively. Comparable crystallographic data for bridging acetylenic units have been well-documented by Gladysz,[4] Bruce,[11] Lapinte,[12] and Akita.[13] The closest intramolecular nonbonded contacts

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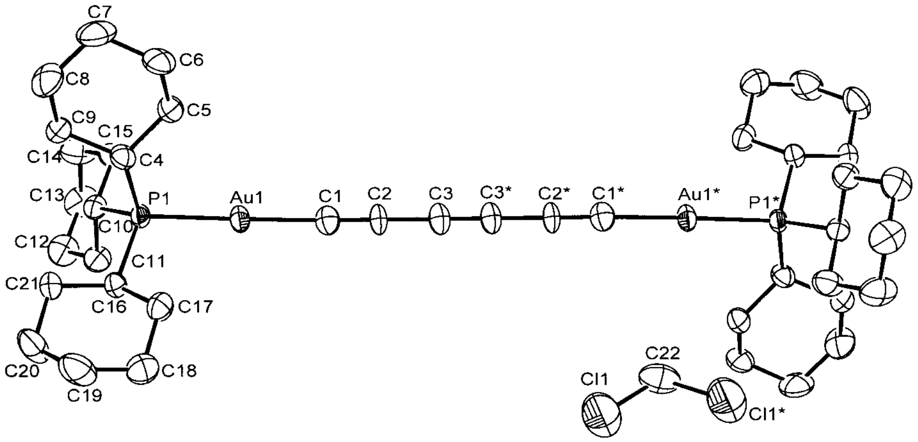

Figure 1. ORTEP plot for **3**·CH_2Cl_2 (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Au(1)–C(1) = 2.011(8), Au(1)–P(1) = 2.292(2), C(1)–C(2) = 1.170(1), C(2)–C(3) = 1.40(1), C(3)–C(3*) = 1.18(1); P(1)–Au(1)–C(1) = 174.1(2), Au(1)–C(1)–C(2) = 172.6(8), C(1)–C(2)–C(3) = 176.7(9), C(2)–C(3)–C(3*) = 179.4(14).

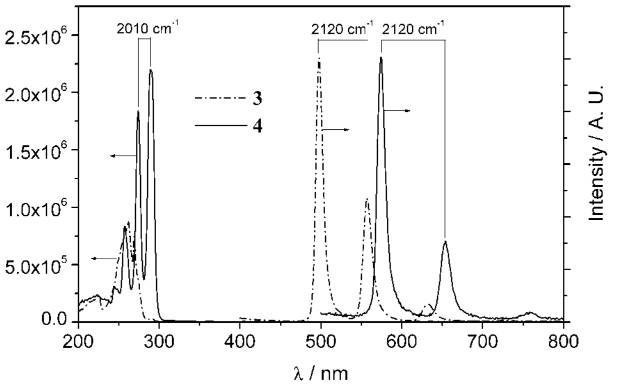

Figure 2. UV absorption and normalized emission spectra for **3** and **4** in CH_2Cl_2 at 298 K.

in this structure are Au(1)–H(5) (1.80 Å) and Au(1)–H(17) (1.92 Å). The solvated CH_2Cl_2 molecule is disordered over an inversion center ((1,0,1) for the reported asymmetric unit). Unlike the lower homologues,[14] no close C–H···π(C≡C) distances (<3.5 Å) were observed.

While the acetylenic $^1(\pi\pi^*)$ transitions for **1**–**3** are buried by red-shifted [5d(Au)] → [6p(Au), π^*(phosphine)] transitions,[10] the highly vibronic absorption at 274–290 nm (with vibrational progression of 2010 cm^{-1}) in the absorption spectrum for **4** in CH_2Cl_2 (Figure 2) can be unambiguously assigned to the dipole-allowed $\pi \rightarrow \pi^*$ transition of the $(C{\equiv}C)_4^{2-}$ bridge. This band is significantly red-shifted when compared to the lowest-energy dipole-allowed transition of the $R(C{\equiv}C)_4R$ (R = CN, ^{t}Bu, Et_3Si) series (λ_{max} < 240 nm);[7] presumably this is due to perturbation arising from Au–C interactions. Due to their limited solubility, the forbidden acetylenic $^3(\pi\pi^*)$ transitions for **3** and **4** have not been detected. Furthermore, complex **4** is unstable in CH_2Cl_2 solution upon prolonged standing. Within 1 h, the absorbances at 290 and 274 nm decrease to half of their original values, accompanied by enhancement of absorption bands at 260 and 252 nm. Similar instability in halogenated solvent has been observed for a Pt(II) tetradiynediyl complex.[15]

Both **3** and **4** are emissive in degassed fluid solutions, rigid matrix, and solid state (Table 1). In CH_2Cl_2 at 298 K, sharp vibronically structured emissions are observed for **3** and **4** with λ_{0-0} lines appearing at 498 and 575 nm, respectively (Figure 2). The large Stokes shifts from the absorption spectra suggest triplet emissions, and this has been confirmed by lifetime measurements of the solid-state emission of **3**. The single vibronic progression of ~2120 cm^{-1} in the emission spectra of **3** and **4** is attributed to ν(C≡C), which is only slightly larger than the vibrational spacings found in the absorption and excitation spectra and indicates minor structural distortion of the $(C{\equiv}C)_n^{2-}$ (n = 3, 4) chains in the $^3(\pi\pi^*)$ excited state. The unambiguously assigned $^3(\pi\pi^*)$ emissions of the $(C{\equiv}C)_n^{2-}$ (n = 3, 4) chains in fluid solution at room temperature have no precedent in the literature, though vibronically structured emissions from Pt(II)–oligoyne conjugated polymer films have been reported by Friend and co-workers.[2] A highly structured emission at a comparable energy level has been observed, in our recent report,[16] for the [(C∧N∧N)-Pt(C≡C)$_4$SiMe$_3$] (HC∧N∧N = 6-phenyl-2,2′-bipyridine) complex in CH_2Cl_2 solution at 298 K. Changes of solvent and temperature have negligible effects on the emission properties of complexes **3** and **4**. There is perfect overlap of the λ_{0-0} bands at 502 nm (for **3**, Figure 3a) and 574 nm (for **4**, Figure 3b) in the 77 K solid-state emission and excitation spectra; hence, the $^3(\pi\pi^*)$ excited states for the bridging $(C{\equiv}C)_3^{2-}$ and $(C{\equiv}C)_4^{2-}$ chains can be estimated to be 19 920 and 17 420 cm^{-1} above the ground states, respectively. It is remarkable that the $^3(\pi\pi^*)$ excited state of the $(C{\equiv}C)_4^{2-}$ bridge can exhibit red emission, despite the fact that it has no discernible absorption band in the visible region; the color of solid **3** and **4** are light yellow.

The unambiguous assignment of the $^3(\pi\pi^*)$ excited states for monodispersed $(C{\equiv}C)_n^{2-}$ units will facilitate spectroscopic characterization of the triplet emissions of $R(C{\equiv}C)_nR$ compounds. The emission data of **3** and **4** together with those of **1** and **2** afford an energy profile

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Table 1. Emission Data for 3 and 4

	complex **3**				complex **4**			
	CH_2Cl_2[a]	toluene glass[b]	solid[a]	solid[b]	CH_2Cl_2[a]	toluene glass[b]	solid[a]	solid[b]
λ_{0-0} (nm)	498	494	505	502	575	571	575	574
λ_{0-1} (nm)	557	554	564	561	655	650	655	653
λ_{0-2} (nm)	632	629	641	639	763	754	760	758
λ_{0-3} (nm)	726	725	740	739				
I_{0-1}/I_{0-0}[c]	0.57	0.62	2.03	1.02	0.42	0.41	0.37	0.45
τ (μs)[d]			25	31				
ϕ[e]	0.027				0.0004			

[a] At 298 K. [b] At 77 K. [c] Defined by peak area. [d] Some lifetime data are unavailable due to lack of absorption for these samples at the laser output wavelengths of 355 and 266 nm. [e] Quinine sulfate in degassed 0.1 N sulfuric acid as reference ($\phi_r = 0.546$).

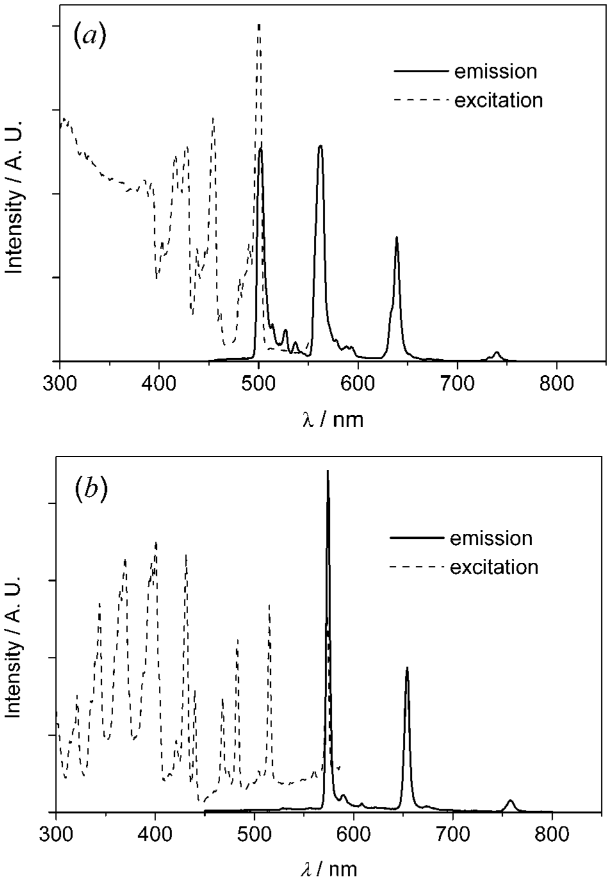

Figure 3. (a) Solid-state emission ($\lambda_{ex} = 427$ nm) and excitation ($\lambda_{em} = 562$ nm) spectra for **3** at 77 K. (b) Solid-state emission ($\lambda_{ex} = 360$ nm) and excitation ($\lambda_{em} = 654$ nm) spectra for **4** at 77 K.

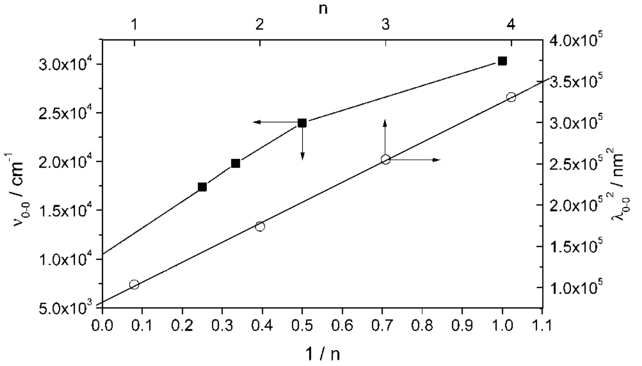

Figure 4. Lewis–Calvin plot ($\lambda_{0-0}^2 = k'n$) (○) and ν_{0-0} energies (cm^{-1}) determined by steady-state emission spectra versus $1/n$ (■) of $Cy_3PAu(C{\equiv}C)_nAuPCy_3$.

for acetylenic $^3(\pi\pi^*)$ excited states. According to the empirical Lewis–Calvin equation,[17] the plot of λ_{0-0}^2 (nm^2) versus number of repeated C≡C units follows a linear relationship with a slope of $k = 7.62 \times 10^4$ nm^2 per triple bond (Figure 4). The average vibrational spacing $\Delta\lambda$ of corresponding adjacent bands in each $Cy_3PAu(C{\equiv}C)_nAuPCy_3$ complex increases with longer chain length. The plot of $\Delta\lambda$ versus n also shows linear behavior ($\Delta\lambda = k'n$) and provides a slope k' of 20 nm per triple bond. On the basis of the plot of ν_{0-0} energy (cm^{-1}) versus $1/n$ (Figure 4), the limiting λ_{0-0} value for the triplet emission of $Cy_3PAu(C{\equiv}C)_\infty AuPCy_3$ is estimated to be 910 nm (11 000 cm^{-1}). When the value 550 nm (18 180 cm^{-1}) is taken from Hirsh[7] as the $^1(\pi\pi^*)$ absorption of $(C{\equiv}C)_\infty^{2-}$, the singlet–triplet splitting of the $(C{\equiv}C)_\infty^{2-}$ chain is estimated to be ~7000 cm^{-1}, which is smaller than related values of ~12 000–13 000 cm^{-1} for butadiyne[6] and Pt(II)–oligoyne conjugated polymers.[3]

Experimental Section

All starting materials were used as received from commercial sources. The compounds $Me_3Si(C{\equiv}C)_nSiMe_3$ (n = 3,[18] 4[19]) were prepared according to literature methods. Elemental analyses were performed by the Institute of Chemistry at Chinese Academy of Sciences, Beijing, People's Republic of China. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. Nuclear magnetic resonance spectra were recorded on Avance400 Bruker FT-NMR spectrometers. Infrared spectra were recorded on a Bio-Rad FT-IR spectrophotometer. UV–vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer. Emission spectra were obtained on a SPEX Fluorolog-2 Model F11 fluorescence spectrophotometer. Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). Errors for λ values (±1 nm) and τ (±10%) are estimated.

General Procedure for Syntheses. To a mixture of $Me_3Si(C{\equiv}C)_nSiMe_3$ (n = 3, 4, respectively; 0.1 mmol) and Cy_3PAuCl (0.2 mmol) in MeOH (30 mL) was added NaOH pellets (0.2 g). The suspension was stirred at room temperature for 1 h. The resulted brown solid was filtered and washed subsequently with water, methanol, and ether. The pure product was obtained after column chromatography (Al_2O_3, CH_2Cl_2) as a light yellow powder.

3: yield 0.085 g, 83%; FAB MS m/z 1027 (M^+); IR (Nujol) ν 2109 (m, C≡C) cm^{-1}; $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 22 °C, TMS) δ 131.3 (d, $^2J_{CP} = 131.4$ Hz, Au*C*), 85.9 (d, $^3J_{CP} = 25.0$ Hz, AuC≡*C*), 75.1 (s, AuC≡C*C*), 32.3 (d, $^1J_{CP} = 28.1$ Hz, Cy), 30.0 (s, Cy), 26.3 (d, $^2J_{CP} = 11.8$ Hz, Cy), 25.2 (s, Cy); $^{31}P\{^1H\}$ NMR

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(CH_2Cl_2, 22 °C, external H_3PO_4) δ 58.2. Anal. Calcd for $C_{42}H_{66}P_2Au_2{\cdot}CH_2Cl_2$: C, 46.45; H, 6.16. Found: C, 46.46; H, 6.24.

4: yield 0.052 g, 50%; FAB MS m/z 1051 (M^+); IR (Nujol) ν 2147 (m, C≡C), 2066 (vw, C≡C), 2007 (vw, C≡C) cm^{-1}; $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 22 °C, TMS) δ 136.0 (d, $^2J_{CP}$ = 122.2 Hz, Au*C*), 87.4 (d, $^3J_{CP}$ = 24.9 Hz, AuC≡*C*), 67.4 (s, AuC≡C*C*), 62.8 (s, AuC≡CC≡*C*), 34.8 (d, $^1J_{CP}$ = 28.0 Hz, Cy), 32.4 (s, Cy), 28.7 (d, $^2J_{CP}$ = 11.6 Hz, Cy), 27.6 (s, Cy); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 22 °C, external H_3PO_4) δ 57.5. Anal. Calcd for $C_{44}H_{66}P_2Au_2$: C, 50.29; H, 6.33. Found: C, 50.00; H, 6.40.

X-ray Crystallographic Determination of 3·CH_2Cl_2. Single crystals of **3**·CH_2Cl_2 were obtained by slow diffusion of Et_2O vapor into a CH_2Cl_2 solution. Crystal data: $C_{43}H_{68}Cl_2P_2Au_2$, M_r = 1111.75, monoclinic, $P2_1/c$ (No. 14), a = 12.420(3) Å, b = 17.719(4) Å, c = 11.283(2) Å, V = 2253.3(8) Å^3, Z = 2, D_c = 1.639 g cm^{-3}, Mo Kα radiation (λ = 0.710 73 Å), μ(Mo Kα) = 6.72 mm^{-1}, $F(000)$ = 1096, T = 301 K, $2\theta_{max}$ = 51°, 3903 independent reflections, 226 variable parameters, R1 = 0.049 ($I > 2\sigma(I)$), wR2 = 0.12 for GOF(F^2) = 0.95.

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Supporting Information Available: Tables giving crystallographic data for **3**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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