

## X-ray-Excited Optical Luminescence (XEOL) and X-ray Absorption Fine Structures (XAFS) Studies of Gold(I) Complexes with Diphosphine and Bipyridine Ligands

Pil-Sook G. Kim,<sup>†</sup> Yongfeng Hu,<sup>‡</sup> Marie-C. Brandys,<sup>†</sup> Tara J. Burchell,<sup>†</sup> Richard J. Puddephatt,<sup>\*,†</sup> and Tsun K. Sham<sup>\*,†</sup>

Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada, and Canadian Light Source, University of Saskatchewan, Saskatoon, Saskatchewan S7N 0X4, Canada

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Synchrotron techniques, X-ray-excited optical luminescence (XEOL) combined with X-ray absorption fine structures (XAFS), have been used to study the electronic structure and optical properties of a series of luminescent gold(I) complexes with diphosphine and bipyridine ligands using tunable X-rays (in the regions of the C and P K-edges and the Au L<sub>3</sub>-edge) and UV from synchrotron light sources. The effects of gold–ligand and aurophilic interactions on the luminescence from these gold(I) complexes have been investigated. It is found that the luminescence from these complexes is phosphorescence, primarily due to the decay of the Au (5d) → PR<sub>3</sub> ( $\pi^*$ ), metal to ligand charge transfer (MLCT) excitation as well as contributions from the conjugated  $\pi$ -system in the bipyridine ligands via the gold–nitrogen bond. The large Au 5d spin–orbit coupling enhances the intersystem crossing. The elongation of the hydrocarbon chain of the diphosphine ligand does not greatly affect the spectral features of the luminescence from the gold(I) complexes. However, the intensity of the luminescence was reduced significantly when the bipyridine ligand was replaced with 1,2-bis(4-pyridylamido)benzene. The aurophilic interaction, as investigated by EXAFS at the Au L<sub>3</sub>-edge, is shown to be only one of the factors that contribute to the luminescence of the complexes.

### Introduction

Gold(I) complexes, including monomers, oligomers, and polymers, often show interesting photophysical and photochemical properties both in solution and in the solid state.<sup>1–8</sup> Gold(I) complexes with diphosphine or diacetylide ligands usually have linear stereochemistry at gold(I),<sup>2–4</sup> and often show short secondary Au–Au interactions (so-called auro-

philic interaction) at distances of 2.8–3.2 Å, whose magnitude is approximately equal to that of a hydrogen bond (6–8 kcal/mol).<sup>6</sup> It is well-established that the origin of the aurophilic interaction, an important example of the attractive interaction between noble metal cations with d<sup>8</sup>, d<sup>10</sup>, or s<sup>2</sup> configurations, is due to the relativistic correlation effects of the heavy metal.<sup>6</sup> The strong photoluminescence of these binuclear complexes is generally assigned as phosphorescence (a large spin–orbit coupling of the Au 5d electrons, ~1.5 eV, greatly enhances the ease of the singlet to triplet intersystem crossing) from the metal-centered or metal-to-ligand charge-transfer excited states (triplets) with long lifetimes. In solution, the excited-state Jahn–Teller distortion and exciplex formation can also affect the photoluminescence.<sup>1</sup>

Luminescent gold(I) complexes are of considerable interest since they can be prepared readily, are stable to air and

\* To whom correspondence should be addressed. E-mail: pudd@uwo.ca (R.J.P.), tsham@uwo.ca (T.K.S.).

<sup>†</sup> University of Western Ontario.

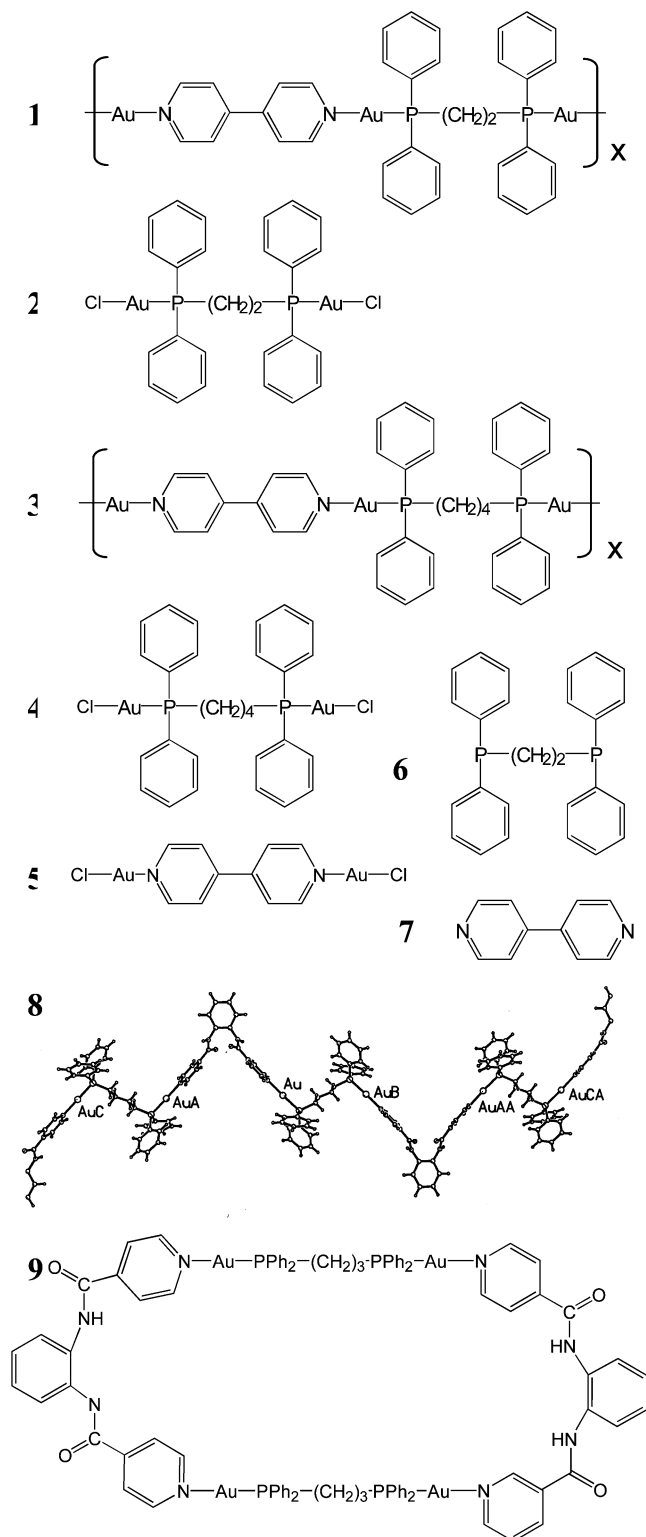
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moisture, and display intense, long-lifetime photoluminescence at room temperature.<sup>9</sup> The emission properties of the gold(I) complexes as a function of the auxiliary ligands and the presence or absence of intramolecular gold(I)–gold(I) interactions have been investigated extensively.<sup>9–13</sup> Ma and co-workers successfully fabricated the dinuclear gold(I) complex  $[\text{Au}_2(\text{dppm})\text{Cl}_2]$  into a device which exhibited a very low turn-on voltage, making it ideal for use in light-emitting diodes.<sup>9</sup> This finding paves the way for using luminescent gold complexes with a triplet-excited state in the fabrication of electroluminescent devices, to complement the established emissive molecules such as  $[\text{Alq}_3]$  ( $q = 8$ -hydroxyquinoline)<sup>14</sup> and  $[\text{Ru}(\text{bipy})_3]^{2+}$  ( $\text{bipy} = 2,2'$ -bipyridine),<sup>15</sup> and organic polymer light emitters (e.g. poly(phenylene vinylene) and derivatives).<sup>16</sup>

This paper reports the investigation into the local structure, electronic properties, and origin of luminescence from gold(I) complexes with diphosphine and bipyridine ligands and the related compounds shown in Figure 1. Of particular interest are the complexes of formula  $[\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{-AuNC}_5\text{H}_4\text{C}_5\text{H}_4\text{NAu}-\}_x]^{2+}[\text{CF}_3\text{CO}_2^-]_{2x}$ , where  $x \gg 1$  (oligomers) and  $n = 2$  (complex **1** in Figure 1) and  $n = 4$  (complex **3**), henceforth denoted  $[\text{Au}_2(\text{dpe})(\text{bipy})]^{2+}$  and  $[\text{Au}_2(\text{dppb})(\text{bipy})]^{2+}$ , respectively [ $\text{dpe} = 1,2$ -bis(diphenylphosphino)ethane;  $\text{dppb} = 1,4$ -bis(diphenylphosphino)butane;  $\text{bipy} = 4,4'$ -bipyridine]. These complexes belong to a family of complexes of gold(I) with diphosphine ligands which have spacer groups of varying hydrocarbon chain lengths (represented by  $n$  in the molecular formula  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ). It has been shown crystallographically that, for  $n = 1$  and  $3$ , the structure is macrocyclic  $[\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{-AuNC}_5\text{H}_4\text{C}_5\text{H}_4\text{NAu}-\}_x]^{2+}[\text{CF}_3\text{CO}_2^-]_{2x}$ ,  $x = 2$ , with 26- and 30-membered rings, respectively, and that the gold(I) atoms adopt the normal, approximately linear geometry about each gold(I) center.<sup>17</sup> The interatomic Au–Au distance (aurophilic interaction) is 3.10 and 5.28 Å for  $n = 1$  and  $3$ , respectively. However, the exact structures of the complexes of interest ( $n = 2$  and  $4$ ) were not determined, since no single crystal suitable for X-ray crystallography could be grown. It is interesting to note that there is a significant difference in the optical properties depending on the chain length. While all complexes exhibit strong emission at around 400 nm in solution, the complexes with odd number chain length show



**Figure 1.** Molecular structures of gold(I) complexes of interest: **1**,  $[\text{Au}_2(\text{dpe})(\text{bipy})]^{2+}$ ; **2**,  $\text{Au}_2(\text{dpe})\text{Cl}_2$ ; **3**,  $[\text{Au}_2(\text{dppb})(\text{bipy})]^{2+}$ ; **4**,  $\text{Au}_2(\text{dppb})\text{Cl}_2$ ; **5**,  $\text{Au}_2(\text{bipy})\text{Cl}_2$ ; **6**,  $\text{dpe}$ ; **7**,  $\text{bipy}$ ; **8**,  $[\text{Au}_2(\text{dppb})(1,2\text{-bis}(4\text{-pyridylamido)benzene})]^{2+}$ ; **9**,  $[\text{Au}_2(\text{dpp})(1,2\text{-bis}(4\text{-pyridylamido)benzene})]^{2+}$  ( $\text{dpe} = 1,2$ -bis(diphenylphosphino)ethane;  $\text{dppb} = 1,4$ -bis(diphenylphosphino)butane;  $\text{bipy} = 4,4'$ -bipyridine ligand,  $\text{dppb} = 1,3$ -bis(diphenylphosphino)propane,  $\text{dppb} = 1,4$ -bis(diphenylphosphino)butane).

only very weak and broad emissions in the solid state. However, the complexes with even number chain length show an intense emission, both in dichloromethane solution, showing an intense single broad peak at 390 nm, and in the

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solid state, exhibiting very intense bipy-like spectral features.<sup>17</sup> Existing evidence leads to a proposed polymeric structure (Figure 1) in which the extent of Au–Au interaction is unknown. Thus, it is desirable to examine this and related complexes in some detail with X-ray excited optical luminescence (XEOL) and X-ray absorption near-edge structure (XANES) at the carbon and phosphorus K-edges as well as Au L<sub>3</sub>-edge extended X-ray absorption fine structures (EXAFS). These techniques probe the local structure of Au and the role of Au–ligand and Au–Au interactions in the luminescence of these complexes. As mentioned above, these binuclear complexes exhibit an interaction between the gold-(I) centers, which has proven to play an important role in their emission properties.<sup>1,9–13</sup> Many experimental<sup>18,19</sup> and theoretical<sup>20–23</sup> studies have indicated that the aurophilic interaction strongly affects the luminescence. For example, Balch and co-workers showed that the formation of extended chains of Au(I) centers that are connected through the Au–(I)–Au(I) interactions contributes to the luminescence of Au–(I) complexes.<sup>18</sup>

This research uses synchrotron techniques which are not widely known, and so it is useful to introduce the XEOL and XAFS techniques and the information that they can yield. XEOL is a photon-in photon-out technique in which the system is excited with X-rays from a synchrotron light source via the excitation of primarily core electrons. The decay of the core hole (via Auger, dominant for elements of low atomic number and X-ray fluorescence) leaves the excited systems with holes in the valence band (HOMO and HOMO-1, etc.) and electrons in the conduction band (LUMO, LUMO+1, etc.). The radiative recombination of the electrons and holes produce luminescence. The advantage of XEOL with synchrotron radiation over convention excitation sources (lamp and laser in the visible and UV region) is that the use of tunable X-ray photons allows for the preferential excitation of a particular element (e.g., C in phosphine) and a particular excitation channel at an absorption edge ( $\pi^*$  resonance associated with the aromatic ring,  $\sigma^*$  associated with C–H bond, etc., at the C K-edge, 1s threshold) since core excitation thresholds are element specific. Thus, with good photon energy resolution that is readily obtainable with modern synchrotron light sources, XEOL can be site (element), chemical (oxidation state), and excitation channel specific.

The optical luminescence intensity, often referred to as photoluminescence yield (PLY), either in zero order (total) or at a selected wavelength, can be used to monitor the absorption spectrum across an edge. This kind of measurement is called optical XAFS, and it can be used to reveal the origin of the luminescence,<sup>16</sup> especially when using soft X-ray excitation.<sup>14–16</sup> The details of the radiative deexcitation in the optical region are complex since the system is in an

excited state (not accessible by UV and visible excitation) after X-ray excitation. In general, all the excited states decay nonradiatively (via a phonon route) and rapidly to the luminescence chromophore (triplet, for example), and this is why XEOL normally exhibits very similar spectral features, which are independent of excitation energy although the relative intensity of the features (branching ratio) is sensitive to the change of excitation energy across an absorption edge where a new excitation channel is created and this new channel decays via a slightly different pathway to the luminescence chromophore. Thus, PLY is very sensitive to the effective coupling of the excited state to the luminescence chromophore (quantum efficiency in producing electron–hole pairs that recombine radiatively), hence, the excitation channel in the vicinity of the edge. In the case of composites or heterostructures, where more than one site is luminescent, discernible excitation energy-dependent XEOL and optical-yield-dependent XANES can be readily observed.<sup>24,25</sup>

XAFS refers to the modulation of the absorption coefficient above an absorption edge of an element in a chemical environment as compared to that of a free atom. It usually refers to the oscillations in the absorption coefficients above an absorption edge. XAFS is conveniently divided into the XANES (up to ~50 eV above the threshold) and the EXAFS, which can extend to 1000 eV above the edge. This division at ~50 eV is arbitrary, but it does reflect the dominating physical processes taking place (multiple scattering in XANES to single scattering in EXAFS) and the corresponding information it can provide.

In the XANES region, dipole-allowed transitions (1s to 2p, for example) turn on when the excitation energy approaches the threshold energy in creating a core hole. As the excitation energy is scanned across the threshold, the core electron is excited to previously unoccupied electronic states that are bound (e.g., LUMO), quasi-bound (shape resonance, or virtual orbitals), and in the continuum (with increasing kinetic energy). The kinetic energy of the photoelectron produced in the XANES region has low kinetic energy and is subject to multiple scattering. Thus, resonances in the XANES can be treated as bound-to-bound and bound-to-quasi-bound transitions, which are sensitive to the unoccupied densities of state (e.g., population of the LUMO) and the molecular symmetry (selection rules). As the kinetic energy of the photoelectrons increases in the EXAFS region, single scattering becomes dominant and information about the interatomic distances, coordination number, and local disorder can be obtained. In this work, Fourier transform is applied to establish the presence or absence of an Au–Au interaction in the radial distribution function.

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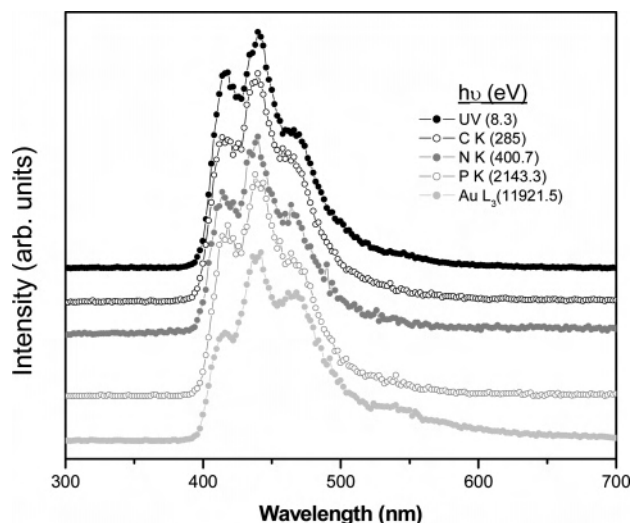
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**Figure 2.** XEOL spectra of complex **1** at various excitation energies ranging from UV (1500 Å, or 8.3 eV) and soft X-rays (C, N, and P K-edges) to hard X-ray (Au L<sub>3</sub>-edge).

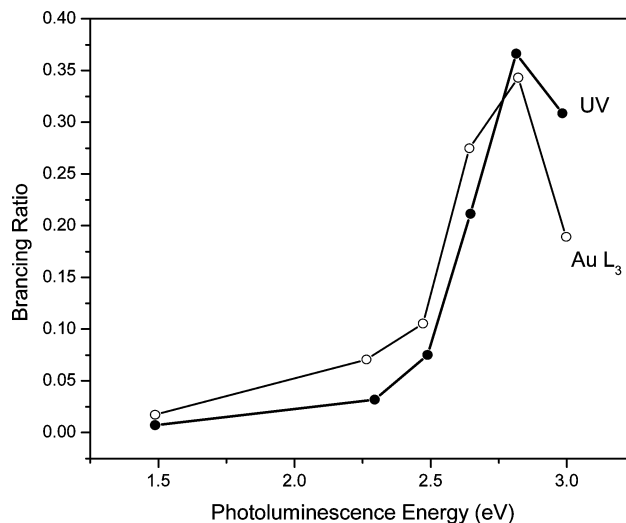
### Experimental Section

The compounds studied are listed in Figure 1 and were prepared by literature methods.<sup>17</sup> The specimens were prepared as thin powder films on indium foil for XANES measurements at the C and P K-edges and on carbon tape for Au L<sub>3</sub>-edge EXAFS in transmission mode. The XANES spectra at the K-edge region of C (275–315 eV) and P (2140–2135 eV) were recorded, respectively, at the Spherical Grating Monochromator (SGM) beamline and the Double Crystal Monochromator (DCM) beamline at the Canadian Synchrotron Radiation Facility (CSRF) situated at the Synchrotron Radiation Center (SRC), University of Wisconsin–Madison. XEOL with VUV excitation (e.g., 8.3 eV) of the inner valence region were made at the SRC Al Seiya beamline. The Au L<sub>3</sub>-edge XAFS were recorded at the Pacific Northwest Consortium-Collaborative Access Team (PNC-CAT), Bending Magnet beamline at the Advanced Photon Source (APS, Argonne, IL). All spectra were normalized by the intensity of the incident beam. The data were processed using the WIN XAS version 3.0 software package.

The XANES spectra were acquired simultaneously in total electron yield (TEY), X-ray fluorescence yield (FLY), and photoluminescence yield (PLY) mode. The monochromatic soft X-ray beam at the SGM beamline has an energy resolution of ~0.3 eV at the carbon K-edge (~285 eV) with a slit size of 100 μm × 100 μm (employed in the measurement for PLY statistics). The XEOL of the complexes were collected with a JY H-10 monochromator equipped with a Hamamatsu photomultiplier tube (943-02) by exciting the complexes with selected photon energies across the C, N, and P K-edges as well as the Au L<sub>3</sub>-edge. The PLY-XANES were obtained by collecting either all the optical photons (zero order) or the partial yield at a selected emission wavelength. It should be reiterated that PLY is sensitive to the chemical environment of the absorbing atom and the excitation channel that may, or may not, couple to the luminescence chromophore effectively, leading to site and excitation channel specificity.<sup>14–16</sup> Consequently, PLY can be used to probe the absorption site responsible for the luminescence.

### Results and Discussion

**Electronic and Optical Properties of Gold(I) Complexes with Diphosphine and Bipyridine Ligands.** Figure 2 shows the XEOL spectra of complex **1** at various excitation energies



**Figure 3.** Branching ratios of luminescence bands with UV and Au L<sub>3</sub> excitations.

ranging from UV (1500 Å, or 8.3 eV) and soft X-rays (C, N, and P K-edges) to hard X-ray (Au L<sub>3</sub>-edge). It can be clearly seen that, regardless of the excitation energies, the luminescence profile (spectral features) remains the same with four well-defined strong peaks at 415 nm (2.98 eV), 440 nm (2.81 eV), 468 nm (2.65 eV), and 500 nm (2.47 eV) and a less intense peak at 539 nm (2.30 eV) in the visible. These observations are consistent with the previous results obtained using a conventional UV emission spectrometer.<sup>17</sup> Brandys and co-workers<sup>17</sup> attributed the origin of the four bands profile to the ligand-based  $\pi-\pi^*$  transitions for bipyridine derivatives since the energy difference between the neighboring bands (1330 cm<sup>-1</sup>) is similar to the vibrational structure of the bipyridine derivatives. In our results, the energy differences between the five bands are ~0.17 eV (1371 cm<sup>-1</sup>). This frequency is very close to the  $-\text{C}=\text{C}-\text{H}$  bending frequency, providing strong evidence for the bipyridine ring being the chromophore. However, since the 4,4'-bipyridine alone is not emissive in solution at room temperature, the presence of the gold(I) centers is likely to have some influence on the luminescence of this complex. The origin very likely lies in the back-donation of the  $\pi$  electrons and the strong spin-orbit coupling of the Au 5d electrons, which greatly facilitates the intersystem crossing from the singlet to the triplet state. We will return to this in conjunction with the Au L<sub>3</sub>-edge EXAFS.

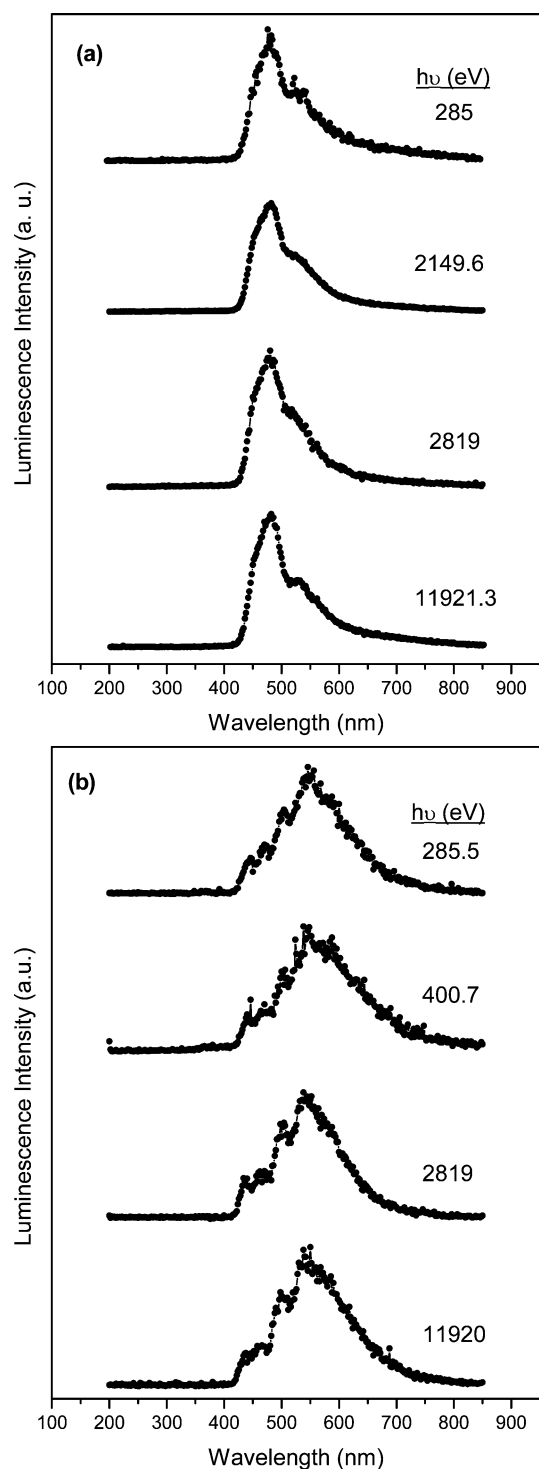
Returning to Figure 2, we see that the relative intensities of the peaks vary. Curve fitting was performed on the photoluminescence spectra to estimate the branching ratio (ratio of area under a specific peak to the total area of all peaks). These values in turn can be used to investigate the effect of excitation energy on the intensity of the luminescence. Each spectrum was fitted with Gaussian peaks using the BGAUSS multiline fitting program version 2.3.<sup>26</sup> The peak widths were fixed to be equal. The result thus obtained is shown in Figure 3 for the UV (8.3 eV) and hard X-ray (11921 eV) excited XEOL, which exhibit a discernible

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difference, while XEOL from other excitations are essentially the same and are in between the two (Figure 2). The peak at 2.81 eV is the most intense (largest transition probability within the vibronic manifold) regardless of excitation energy. It is interesting to note that, with UV excitation, the branching ratio of the peak at 2.98 eV is the most intense of all excitation energies, by a factor of  $\sim 1.5$  compared to the others at the expense of the lower energy emissions, while the XEOL excited with hard X-ray is the least. In contrast, with hard X-ray excitation ( $\sim 11921$  eV), the branching ratio of the peak at 2.65 eV is the reverse. This might indicate that the creation of a shallow hole in the valence band and an Au core hole has influence on the relative intensity of the vibronic manifold, since UV excitation tends to populate electrons from HOMO, HOMO-1 to LUMO, LUMO+1, etc., while Au 2p excitation tends to populate d holes in the valence band. The quantitative details of the variation in relative intensity of the bands will require theoretical calculations and further investigation.

Let us now consider the binuclear gold(I) complexes containing either the diphosphine or the bipyridine and a chloride ligand. The luminescence spectra of complexes **2** and **5** are shown in Figure 4a,b, respectively. Complex **2** exhibits two emission maxima at  $\sim 470$  and 530 nm, regardless of excitation energy. The branching ratios vary slightly, but no significant difference was observed. The emission profile of complex **2** is in good agreement with results reported by Jones and co-workers<sup>27</sup> except for the additional peak at 530 nm. In fact, the luminescence profile of complex **2** is identical with that for  $[(C_6H_5)_3PAuCl]$ , which was reported previously.<sup>28</sup> The emission is a phosphorescence process due to a metal to ligand charge transfer (MLCT) excitation, having mostly Au 5d  $\rightarrow$  PR<sub>3</sub> ( $\pi^*$ ) character. Complex **5** shows a strong emission in the region 400–700 nm with vibronic structures similar to complex **1**. The origin of the luminescence is due to a bipyridine ring  $\pi$ – $\pi^*$  excitation, probably with some N  $\rightarrow$  Au charge transfer. It is interesting to note that, in complex **2**, the phenyl ring is interacting with gold indirectly via the phosphorus atom, which acts primarily as a good  $\sigma$  donor, while, in complex **5**, the bipyridine ring interacts with gold directly via the nitrogen atom which is part of the aromatic ring. Thus, the  $\pi$  system of the ring can interact with Au effectively enhancing triplet conversion and so increasing the luminescence intensity. The sum of the luminescence for complexes **2** and **5** has a good resemblance to that of complex **1**.

We now return to the oligomers. Complexes **3** and **4** were prepared by replacing dppe in complexes **1** and **2** with dppb. This was performed to explore the effect of bridging chain elongation on the luminescence of the binuclear gold(I) complexes. Figure 5a,b shows the XEOL of complexes **3** and **4** (analogous to their shorter chain counter parts complexes **1** and **2**), respectively, collected with various excitation energies from C K-edge (285 eV) to Au L<sub>3</sub>-edge



**Figure 4.** XEOL spectra of (a) complex **2** and (b) complex **5** at various excitation energies ranging from C K-edge to Au L<sub>3</sub>-edge.

(11921 eV). The XEOL from complex **3** exhibits four emission maxima equivalent to complex **1**, but the luminescence intensities were not as strong as in complex **1**. As in complex **1**, the branching ratio varies somewhat depending on the excitation energy. Complex **4** shows the same luminescence behavior as complex **2** with two main emission maxima at the same wavelength, regardless of the excitation energies. One interesting observation is that, in addition to the main emission peaks, complex **4** exhibits a weak emission at around 300 nm. Overall, the similar luminescence behavior

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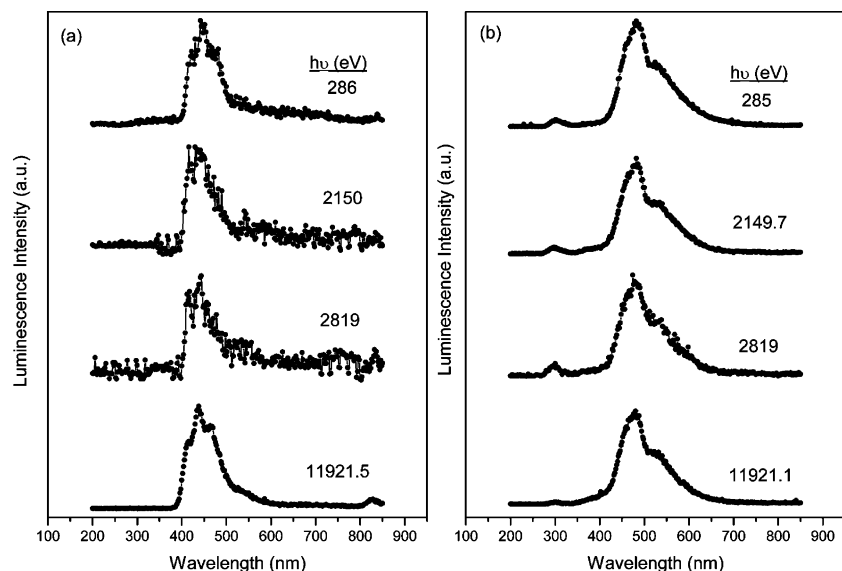


Figure 5. XEOL spectra of (a) complex **3** and (b) **4** at selected excitation energies.

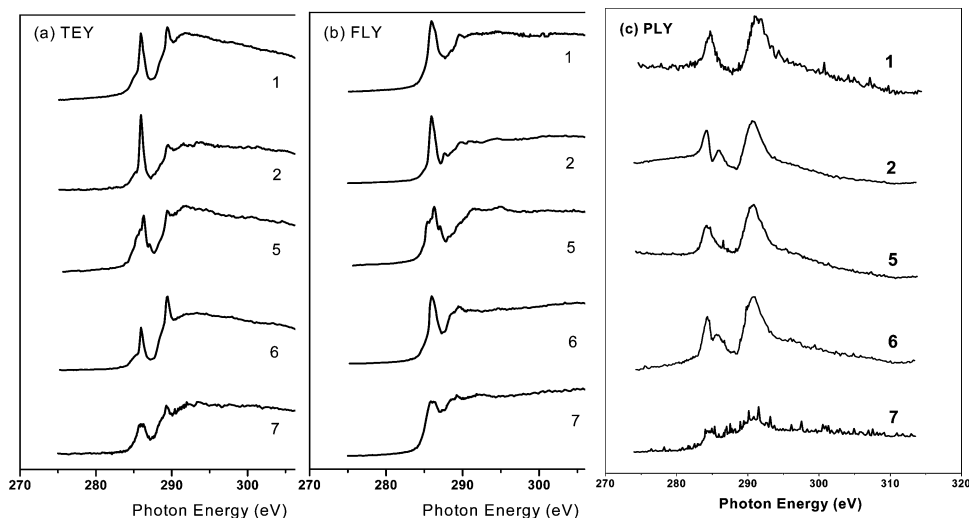


Figure 6. C K-edge XANES of complex **1**, **2**, and **5** in (a) TEY, (b) FLY, and (c) zero-order PLY compared to that of the free ligands, dppe (**6**) and bipy (**7**).

of complexes **1** and **3**, as well as complexes **2** and **4**, suggests that the addition of a methylene spacer group to the bridging phosphine group does not alter the spectral pattern of the gold(I) complex. The increase in the spacer group length appears to have reduced the luminescence efficiency. This may be due to different packing of the chain in the solid state allowing for more efficient quenching of the luminescence in the longer chains.

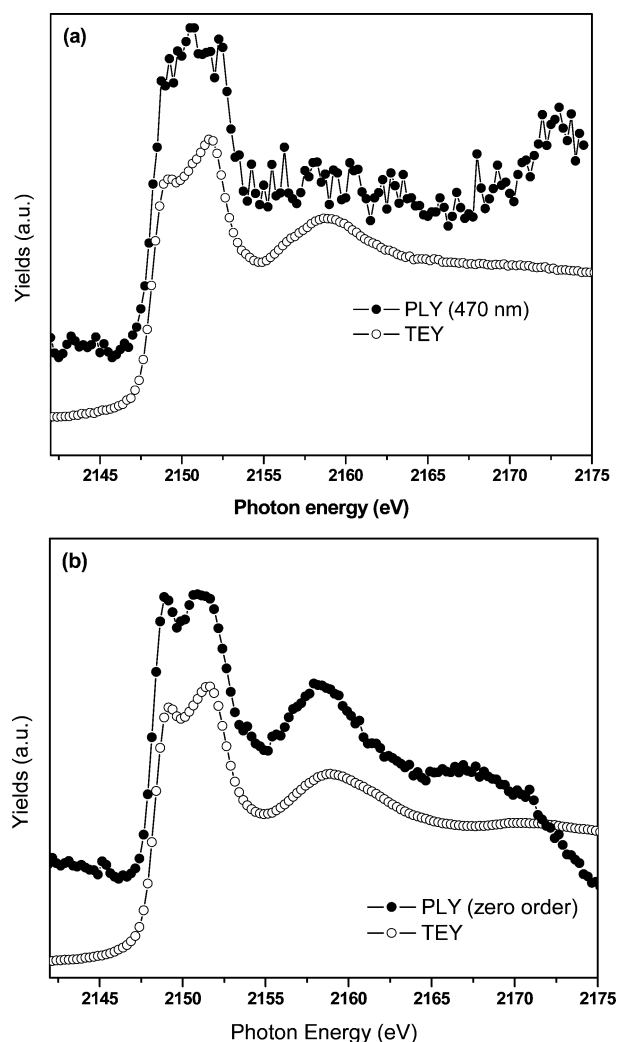
Figure 6 shows the C K-edge XANES of complexes **1**, **2**, and **5** acquired in (a) TEY, (b) FLY, and (c) PLY modes compared to that of the free ligands, dppe (**6**) and bipy (**7**). Let us concentrate on the TEY for the moment, which represents the absorption spectrum. The C K-edge XANES of complexes **1**, **6**, and **7** have been previously reported,<sup>25c</sup> and they are shown here for comparison. Typically, the C K-edge of unsaturated organic molecules exhibits two types of main transitions, (i) low energy ( $\sim 285\text{--}286$  eV) features that are usually sharp and intense represent the C 1s  $\rightarrow \pi^*$  (bound state) transition and the broad transition at higher energy ( $\sim 290\text{--}292$  eV) which represents a C 1s  $\rightarrow \sigma^*$  (quasi

bound state involving carbon–carbon interaction) transition and (ii) the weak resonances in between associated with the C 1s  $\rightarrow \sigma^*$  transition of the C–H bond ( $\sim 289$  eV). It is apparent from Figure 6 that all spectra exhibit a strong absorption at 285.5 eV and a weak shoulder at 284.6 eV as observed in the spectra of complexes **1**, **2**, and **5**. These absorption peaks are attributed to C 1s to  $\pi^*$  transitions of nonequivalent carbons on the dppe phenyl rings and bipy rings. Qualitatively, one can determine which absorption peak arises predominantly from which ligand by using Figure 6 alone. The observation of a sharp  $\pi^*$  resonance in dppe and a less intense  $\pi^*$  resonance, as well as a shoulder at lower photon energy in bipy, can be attributed to a more significant chemical inhomogeneity among the carbon atoms in the bipy ring. Thus, the XANES of the bipy ligand reveals that there is more than one 1s to  $\pi^*$  transition, and this can be attributed to the existence of chemically nonequivalent carbons on the bipy ligand, while such an effect in dppe is small and unresolved with the experimental energy resolution used in these experiments. The difference arises from the greater

electronegativity of nitrogen compared to phosphorus, the incorporation of nitrogen into the aromatic ring, and that the carbon atoms directly bonded to the more electronegative nitrogen are associated with the higher energy transition. From these results it can be concluded that the weak  $\pi^*$  shoulder in Figure 6a in the C K-edge XANES spectra of the gold(I) complexes arises mainly from the bipyridine ligand.

Figure 6b shows the corresponding FLY spectrum at the C K-edge. They are similar to the TEY in spectral features with some intensity variations. It should be noted that, under ideal conditions (thin film and homogeneous sample), the TEY and FLY should be identical. In practice, FLY tends to suffer from self-absorption (thickness effect), which broadens the sharp peaks. We see from Figure 6b that strong absorptions at 285.5 eV are still noticeable, although absorption around 290 eV, which represents the  $1s$  to  $\sigma^*$  transition (C–H), is suppressed. The most interesting feature is seen in Figure 6c, which compares the zero order (collecting all the photons) PLY of all the compounds at the C K-edge. It must be noted that PLY and FLY have comparable sampling depths, which are significantly larger than that of TEY. Thus, a noticeable difference in these two yields indicates that the PLY is sensitive to the excitation channel at the C K-edge. They all show two broad bands at the region of  $\pi^*$  and  $\sigma^*$  resonance. The sharp C–H  $\sigma^*$  ( $\sim 289$  eV) cannot be detected. Complexes **2** and **6** (with a dppe ligand) both exhibit a kink in the region of the  $\pi^*$  resonance ( $\sim 285$  eV) resulting from a significant drop in quantum efficiency of radiative electron–hole pair production at this transition, while this is not seen in the PLY spectra of complexes **5** and **7** (bipyridine) which show a resemblance to complex **1**. This observation indicates that the  $\pi$  system from the phenyl rings in the phosphine ligand does not couple to the luminescence chromophores effectively while the conjugated  $\pi$  system in the bipyridine ligands does. This is confirmed by replacing the phenyl rings with methyl groups, which showed no alteration in the emission profile.<sup>27</sup>

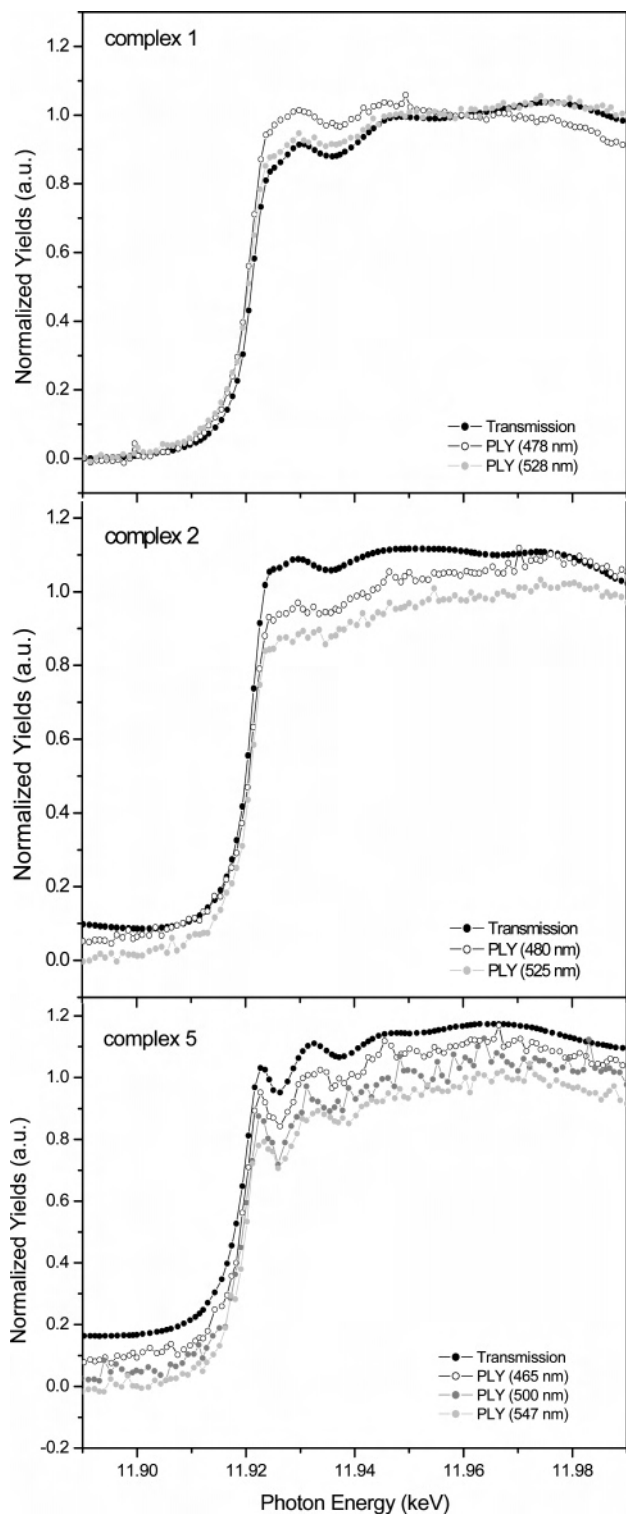
Figure 7 shows the phosphorus K-edge XANES spectra of (a) complex **1** and (b) complex **2** acquired in TEY and partial PLY modes. The P K-edge XANES probes the excitation of electrons from P  $1s$  to an unoccupied p states in the LUMO and above. Thus, the decay of the core hole will generate holes in the valence band and electrons in the LUMO and above. Complexes **1** and **2** exhibit the same XANES features due to the common molecular arrangements around the phosphorus atoms in both complexes. In comparison with the dppe ligand, the white lines (intense resonance at the threshold) in the complex are blue-shifted by 0.5 eV, indicating that phosphorus is a net donor to gold. The partial PLY spectra exhibit the same spectral features as the TEY spectra for both complexes. This indicates that local excitations at the P K-edge are strongly coupled to the luminescent chromophore. Thus, the emission can be assigned to the decay of an excited state having both P and Au character. This is also supported by the observation of an intense Au  $L_{3,2}$ -edge white line for these complexes (to be discussed below) indicating that the



**Figure 7.** Phosphorus K-edge XANES of (a) complex **1** and (b) complex **2** in TEY and partial zero-order PLY.

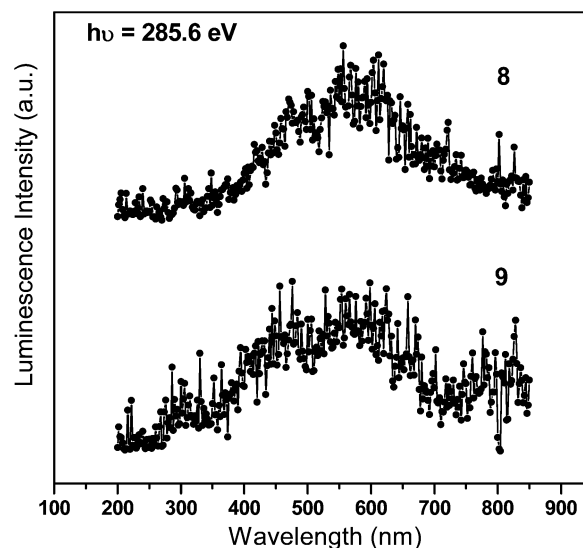
P–Au–Cl moiety has a high density of unoccupied states of Au d character.

Figure 8 shows the Au  $L_{3,2}$ -edge XANES of complexes **1**, **2**, and **5** in transmission and partial PLYs. The XANES spectra of complexes **1** and **2** show similar broad resonances in the whiteline region indicating that there are probably overlapping d states (the area under the whiteline is proportional to the Au 5d hole population). As shown in Figure 1, Au is bonded to P and N in complex **1** but to P and Cl in complex **2**. Thus, the similarity comes from the presence of strong  $\pi$  back-bonding from P to Au in complex **2** which offsets the charge transfer from Au to Cl. Complex **5**, with bipyridine and chloride ligands, shows distinctly different features with a sharp whiteline at the threshold indicating the unoccupied Au 5d states are more localized. What is common to all three complexes is that the partial PLY exhibits the same profiles as the transmission spectrum, confirming the strong involvement of the gold atoms in the luminescence of these complexes. If the Au 5d states were not involved in the luminescence chromophore, then the PLY could drop at the edge since the creation of the  $2p_{3/2}$  core hole also provides a new X-ray fluorescence decay channel.



**Figure 8.** Au  $L_3$ -edge XANES of complex **1**, **2**, and **5** in transmission and partial PLYs.

This analysis of the C and P K-edge and Au  $L_3$ -edge XANES and XEOL indicates that the luminescence of the gold(I) complexes **1**, **3**, and **5** is primarily from the bipyridine ligand. In complexes **2** and **4**, which do not contain a bipyridine ligand, the luminescence arises primarily from excited-state with  $P \rightarrow Au(I)$  ligand to metal charge transfer (LMCT).<sup>23</sup>



**Figure 9.** XEOL spectra of complex **8** and **9** excited at the C K-edge  $\pi^*$  resonance (285.6 eV).

**Effect of Different Ligands on the Luminescence of Gold(I) Complexes.** We have also studied the effect of different ligands on the luminescence of the gold(I) complexes. In this study, the 4,4'-bipyridine ligand was replaced with the 1,2-bis(4-pyridylamido)benzene ligand, LL, and the chain length of the diphosphine ligand was also varied to  $n = 3$  (dppp = 1,3-bis(diphenylphosphino)propane) and 4 (dppb = 1,4-bis(diphenylphosphino)butane). As shown in Figure 1, complex **8** exists as polymeric cations with repeat units of  $\{[-LL-Au-dppb-Au-]\}_x^{2+}$ . Through interchain amide hydrogen bonds, this complex results in a three-dimensional network.<sup>27</sup> Complex **9**, with one less methylene spacer group in the diphosphine group than complex **8**, has a very different structure, which is the 42-membered double ring tetracation with a steplike conformation.<sup>30</sup>

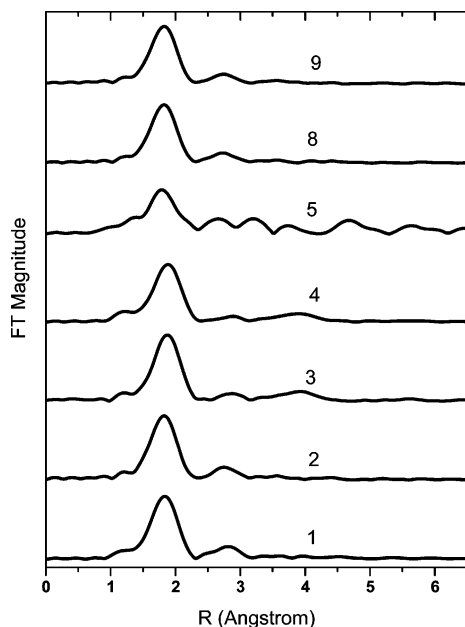
The XEOL spectra of complexes **8** and **9** are shown in Figure 9. These complexes show a very weak and broad luminescence in the region from 400 to 700 nm in the solid state. The difference in the luminescence properties of these complexes with two different ligands is the more extended region of luminescence at both shorter and longer wavelengths for the ring compound. The broad features in the emission with some fine structures indicate the involvement of the vibronic transitions associated with aromatic ring. Further investigation is required to assign these features.

**Aurophilic Interaction and the Luminescence of Gold(I) Complexes: Au  $L_3$ -Edge EXAFS.** It has been established that the Au–Au aurophilicity has significant influence on the excited-state properties for the binuclear Au(I) complexes that produce the lower energy emission at  $\sim 2.4$ – $2.7$  eV with the metal-centered transition character.<sup>23</sup> The Au–Au interactions are typically identified by X-ray crystallography. However, since X-ray-quality crystals were not always obtained, we utilized EXAFS to investigate Au–Au interactions and to correlate the aurophilicity to the lumi-

(29) Burchell, T. J.; Eisler, D. J.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2003**, 2228.

(30) Jones, P. G. *Gold Bull.* **1981**, *14*, 102.





**Figure 10.** Fourier transforms magnitude ( $k^2$ -weighted) versus distance for complexes **1–5**, **8**, and **9**.

nescence of these complexes at room temperature. The  $k^2$ -weighted Fourier transform of the EXAFS data are shown in Figure 10 for complexes **1–5**, **8**, and **9**. Corresponding  $k^2\chi(k)$  vs  $k$  EXAFS data for complexes **1–5**, **8**, and **9** are available online as Supporting Information. In all radial distributions, there is a strong distinct peak at  $1.80 \pm 0.02$  Å. This peak represents the overlap of the Au–P and Au–N bonds. A less intense peak appears at  $\sim 2.90$  Å (the corresponding phase corrected Au–Au distance is  $3.10 \pm 0.05$  Å) in all complexes, and this value lies within the range of Au–Au interactions.<sup>30</sup> Our XEOL results indicate that the gold(I) complexes, with diphosphine and bipyridine ligands (complexes **1–5**), exhibit strong luminescence while the complexes with bis(amido)bipy ligand (complexes **8** and **9**) show very weak luminescence. The presence of aurophilic interactions in the entire series of complexes does not support the hypothesis that the luminescence of these complexes correlates with the presence of aurophilic interaction, as Jones and co-workers suggest on the basis of their EXAFS studies on binuclear gold(I) complexes at liquid-helium temperature.<sup>30</sup> Such a correlation may exist within a series of related compounds, but the universality of this correlation awaits further investigation.

## Conclusions

XEOL and XAFS studies of gold(I) complexes with diphosphine (dppe), bipyridine (bipy), and bis(amido)bipy ligands were performed at the carbon and phosphorus K-edges and the gold  $L_3$ -edge. Complexes with both dppe and bipy ligand showed intense luminescence with a well-defined four peak vibronic profile, characteristic of emission from the gold–bipyridine unit where the large spin–orbit coupling of the Au 5d electrons facilitates the emission. The emissive state can be populated either directly or indirectly from the Au  $\rightarrow$  P LMCT excited state. The effect of chain elongation of the diphosphine ligand  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  was also examined, and it was found that increasing the chain length, from  $n = 2$  to  $n = 4$ , showed no alteration in the luminescence property. However, by replacement of the bipyridine ligand with 1,2-bis(4-pyridylamido)benzene, the intensity of luminescence of the gold(I) complexes was reduced significantly. This was due to the bulky bis(4-pyridylamido)benzene ligand which prevents the formation of Au–Au aurophilic interaction that is known to couple to the luminescence of the gold(I) complexes. Moreover, the role of the aurophilic interaction to the luminescence of the gold(I) complexes was investigated by EXAFS at the Au  $L_3$ -edge. All complexes showed weak Au–Au interactions at around 3.10 Å, but the intensity of the luminescence was variable. Thus, our results suggest that the aurophilic interaction is not the only factor that is responsible for the luminescence.

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**Supporting Information Available:** The Au  $k^2\chi(k)$  vs  $k$  EXAFS data for complexes **1–5**, **8**, and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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