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# The Lowest Excited State of Brightly Emitting Gold(I) Triphosphine Complexes

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The strongly luminescent neutral gold(I) triphosphine complexes [Au(dipnc)($PPh_3$)] and [Au(dppnc)($PPh_3$)] with dipnc = 7,8-bis(diisopropylphosphino)-*nido*-carborane ($[(PiPr_2)_2B_9H_{10}C_2)]^-$) and dppnc = 7,8-bis(diphenylphosphino)-*nido*-carborane ($[(PPh_2)_2B_9H_{10}C_2]^-$) are studied in a wide range of temperatures of $1.5 \leq T \leq 300$ K. Analysis of the emission decay dynamics provides detailed information about the lowest triplet state. In particular, the magnitude of zero-field splitting of the emitting state is determined to be 47 and 29 $cm^{-1}$ for [Au(dipnc)($PPh_3$)] and [Au(dppnc)($PPh_3$)], respectively. The emission decay times of the individual triplet substates lie in the range of 4 to 130 $\mu$s. The observed photophysical properties suggest that the molecular orbitals involved in the lowest electronic transitions exhibit, beside gold orbitals, considerable contributions from nonmetallic ligand orbitals. OLED or sensor application of these complexes is suggested.

## 1. Introduction

Luminescent organo-transition metal complexes have received increasing attention, as they represent materials for opto-electronic applications. In particular, organic light emitting devices (OLEDs) employing such compounds exhibit superior efficiencies, exceeding those obtained with purely organic fluorescent materials.[1−8] This is a consequence of spin−orbit coupling (SOC) of the heavy metal ion. Thus, both singlet and triplet excitations induced by the electroluminescence process can be harvested according to the triplet harvesting[1,3,4a] and the recently discovered singlet harvesting[4b] mechanisms. At present, cyclometalated Ir(III) or Pt(II) complexes seem to be the first choice for triplet emitter materials for OLED applications.[5−8] However, difficulties encountered with these compounds for deep-blue[9] or white light emission stimulate the research of triplet emitters with other central metal ions. In this respect, Au(I) complexes and clusters represent interesting groups of luminescent materials. One class of such compounds includes three-coordinate complexes of the type $[Au(L)_3]^{n+}$ with L representing aromatic or aliphatic phosphine ligands.[10−17] These compounds often exhibit intense luminescence in the visible spectral range. The lowest electronic transitions responsible for the observed emissions have been considered to be spin-forbidden, strongly involving Au-centered 5d and 6p orbitals.[11−14] In the present work, we report luminescence properties of the neutral three-coordinate gold(I) complexes [Au(dipnc)($PPh_3$)] and [Au(dppnc)($PPh_3$)] (with dipnc = 7,8-bis(diisopropylphosphino)-*nido*-carborane ($[(PiPr_2)_2B_9H_{10}C_2)]^-$) and dppnc = 7,8-bis(diphenylphosphino)-*nido*-carborane ($[(PPh_2)_2B_9H_{10}C_2)]^-$) and $PPh_3$ = triphenylphosphine, Figure 1). These strongly luminescent compounds have

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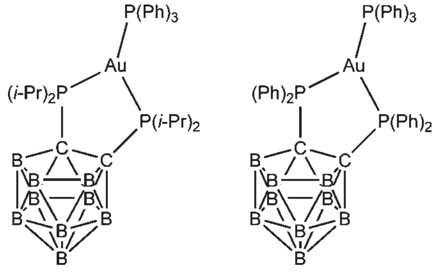

[Au(dipnc)(PPh$_3$)] [Au(dppnc)(PPh$_3$)]

**Figure 1.** Structure formulas of the studied compounds, *i*-Pr = isopropyl, Ph = phenyl group.

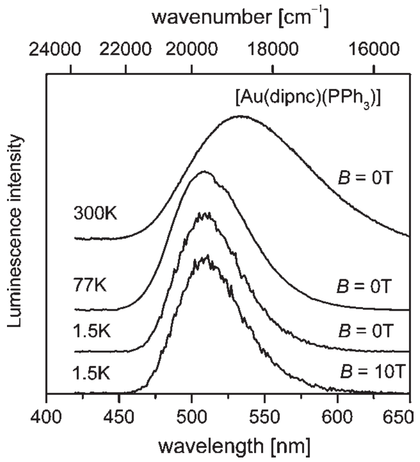

**Figure 2.** Luminescence spectra of [Au(dipnc)(PPh$_3$)] measured in MTHF ($c \approx 10^{-5}$ mol/L) at different temperatures. The lowest spectrum is recorded under application of a high magnetic field ($B$ = 10 T). Excitation: $\lambda_{exc}$ = 337 nm.

already been investigated,[16,17] however, without considering the emission properties in detail.

## 2. Results and Discussion

[Au(dipnc)(PPh$_3$)] and [Au(dppnc)(PPh$_3$)] display intense green luminescence also at ambient temperature. Figure 2 shows the emission spectra of [Au(dipnc)(PPh$_3$)] measured in 2-methyltetrahydrofuran (MTHF) at ambient temperature, at 77 K, and at 1.5 K. Characteristic emission data are summarized in Table 1. At ambient temperature, the emission spectra are very broad. Upon cooling from 300 to 77 K, the half-width becomes significantly smaller and the band maximum shifts by about 1000 cm$^{-1}$ to higher energy. Such a behavior is often observed and can be related to the hindered reorganization of the solvent molecules in frozen samples as compared to the liquid phase. Further temperature reduction does not change the spectra significantly. The emission decay times $\tau$ lie in the range of several microseconds, which is characteristic of spin-forbidden triplet–singlet transitions of organo-transition metal compounds. The triplet nature of the emitting state will be further substantiated below. It is stressed that emission quantum yields of 75 and 50% found for [Au(dipnc)(PPh$_3$)] and [Au(dppnc)(PPh$_3$)] in poly(methyl methacrylate) (PMMA), respectively, are relatively high.

**Table 1.** Luminescence Properties of [Au(dipnc)(PPh$_3$)] and [Au(dppnc)(PPh$_3$)]

| compound | [Au(dipnc)(PPh$_3$)] | [Au(dppnc)(PPh$_3$)] |
|---|---|---|
| 300 K: $\lambda_{max}/\tau$ [a] | 525 nm/12 $\mu$s | 534 nm/8 $\mu$s |
| 77 K: $\lambda_{max}/\tau$ [b] | 508 nm/20 $\mu$s | 497 nm/15 $\mu$s |
| $\phi_{PL}$ (300 K) [a] | 75% | 50% |

[a] Measured in PMMA, $c \approx 1$ wt %, *relative* experimental error ± 10%. [b] Measured in MTHF, $c \approx 10^{-5}$ mol/L.

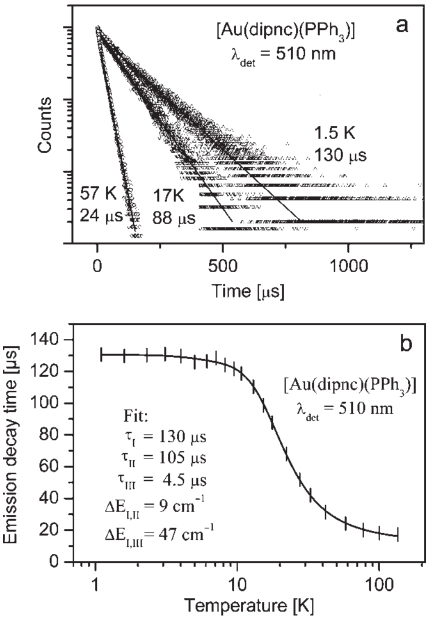

**Figure 3.** (a) Representative emission decay curves of [Au(dipnc)(PPh$_3$)] in MTHF at different temperatures. (b) Plot of the measured emission decay time of [Au(dipnc)(PPh$_3$)] versus temperature. The solid line represents a fit of eq 1 to the experimental data. The resulting fit parameters are reproduced in the diagram.

Even at $T$ = 1.5 K, the emission spectra are unresolved. Thus, information about the individual substates of the emitting triplet state T$_1$ is not directly available. Nevertheless, it is possible to extract valuable information from the temperature dependence of the luminescence decay time. As depicted in Figure 3a, the emission decay is almost monoexponential, indicating a fast thermalization between the substates of the emitting triplet state (T$_1$ state) and a relatively uniform zero-field splitting (ZFS) pattern of the investigated compounds in frozen glassy solutions. Interestingly, for other compounds, for instance, for [Ir(dFppy)$_2$(pic)][18] (dFppy = 2-(4′,6′-difluorophenyl)pyridinate and pic = picolinate) and [Ir(btp)$_2$(acac)][19] (btp = 2-(2′-benzothienyl)pyridinate and acac = acetylacetonate) studied in dichloromethane and dichloromethane, respectively, the emission decay curves measured at low temperatures under non site-selective conditions deviate considerably from a monoexponential decay. This behavior being different from that observed for the studied Au complexes, has been related to slightly different interactions between the emitting complexes and the matrix molecules giving different spectral sites and thus different ZFSs.[18,19]

In Figure 3b, the emission decay times of [Au(dipnc)(PPh$_3$)] are plotted versus temperature. Below about 8 K, one observes a plateau with a decay time of 130 ± 3 $\mu$s. With increasing temperature, the decay time becomes shorter and rapidly decreases to 17 $\mu$s at $T$ = 135 K. Such a behavior is

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often observed for luminescent organo-transition metal compounds and results from an increasing population of higher triplet substates with increasing temperature.[18-21] Since each of the three substates of $T_1$ (I, II, and III) experiences different spin−orbit couplings to higher singlet states, the corresponding electronic transitions to the ground state are differently allowed, and each substate emits according to its individual decay time. Provided that the spin−lattice relaxation rates[22,23] between the $T_1$ substates are significantly larger than the decay rates of the individual substates of $T_1$, the emission decays at a given temperature with an average time constant $\tau_{av}$ according to:[18,20,21,24]

$$k_{av} = \frac{1}{\tau_{av}} = \frac{k_I + k_{II}\,e^{-\Delta E_{I,II}/k_B\cdot T} + k_{III}\,e^{-\Delta E_{I,III}/k_B\cdot T}}{1 + e^{-\Delta E_{I,II}/k_B\cdot T} + e^{-\Delta E_{I,III}/k_B\cdot T}} \quad (1)$$

wherein $\tau_I = 1/k_I$, $\tau_{II} = 1/k_{II}$, and $\tau_{III} = 1/k_{III}$ are the emission decay times of the respective substates I, II, and III and $k_I$, $k_{II}$, and $k_{III}$ are the decay rates of the individual $T_1$ substates. $k_B$ is the Boltzmann constant, and $\Delta E_{I,II}$ and $\Delta E_{I,III}$ are the energy separations between the substates I and II and substates I and III, respectively. If the observed emission decay time is identified with $\tau_{av}$, a quantitative analysis can be carried out by a fitting procedure of eq 1 to the experimental data (Figure 3). The energy separations between the substates are determined to $\Delta E_{I,II} = 9 \pm 1$ cm$^{-1}$ and $\Delta E_{I,III} = 47 \pm 5$ cm$^{-1}$ (total ZFS). For the individual decay times, values of $\tau_I = 130 \pm 3$ $\mu$s, $\tau_{II} = 105 \pm 8$ $\mu$s, and $\tau_{III} = 4.5 \pm 1$ $\mu$s are found. The decay time $\tau_I$ resulting from the fit is equal to the decay time measured for $T = 1.5$ K. This is expected, since at low temperatures, only the lowest substate I is populated. At higher temperatures, the average decay time is determined by the relative population of the higher lying substates and their individual decay rates. A corresponding analysis for [Au(dppnc)(PPh$_3$)] leads to ZFS parameters of $\Delta E_{I,II} = 4.5 \pm 1$ cm$^{-1}$ and $\Delta E_{I,III} = 29 \pm 4$ cm$^{-1}$ and decay times of $\tau_I = 122 \pm 4$ $\mu$s, $\tau_{II} = 35 \pm 3$ $\mu$s, and $\tau_{III} = 4 \pm 1$ $\mu$s. These results are summarized in energy level diagrams for the two compounds as reproduced in Figure 4.

In addition, the luminescence behavior of [Au(dipnc)(PPh$_3$)] and [Au(dppnc)(PPh$_3$)] has been investigated under high magnetic fields. Application of magnetic flux densities up to $B = 10$ T (at $T = 1.5$ K) does not lead to any noticeable change in the emission spectra in the scope of resolution obtained (Figure 2). Apparently, the relatively small Zeeman shifts of the $T_1$ sublevels are not sufficient to induce significant shifts of the broad and unresolved emission spectra. The fact that no change of the emission band envelope is observed indicates that the vibronic mechanisms responsible for the radiative deactivations from the three triplet substates as well as the involved vibrational modes are similar. (A completely different situation is described in refs 21, 25, and 26.) On the other hand, an external magnetic field influences the emission decay time, as depicted in Figure 5.

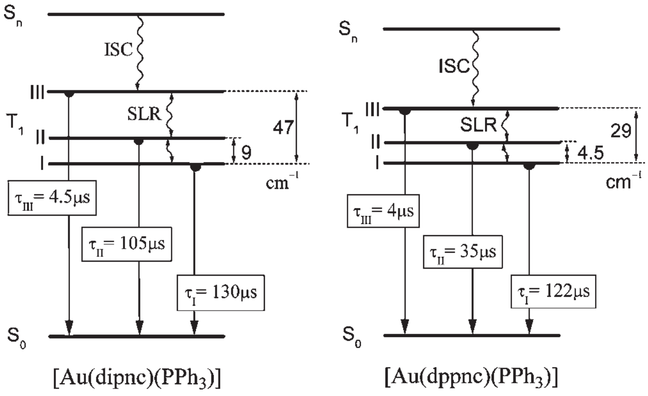

**Figure 4.** Energy level diagrams and emission decay times for the three substates of the lowest triplet state of [Au(dipnc)(PPh$_3$)] and [Au(dppnc)(PPh$_3$)] in MTHF ($c = 10^{-5}$ mol/L). ISC and SLR symbolize intersystem crossing and spin−lattice relaxation processes, respectively, responsible for the population of the $T_1$ substates and the thermalization between them.

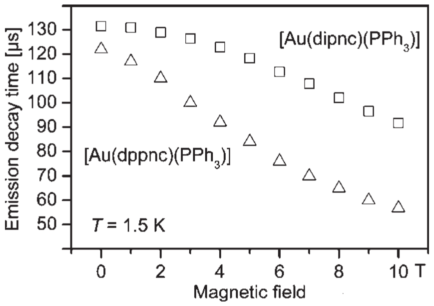

**Figure 5.** Luminescence decay times of [Au(dipnc)(PPh$_3$)] and [Au(dppnc)(PPh$_3$)] in MTHF at $T = 1.5$ K versus a high external magnetic field strength. The decay times were measured after pulsed excitation at $\lambda_{exc} = 337.1$ nm at different magnetic field strengths (flux densities $B$) and they were monoexponential for all B-fields studied. The emission was recorded at $\lambda_{em}$ = 510 and 500 nm for [Au(dipnc)(PPh$_3$)] and [Au(dppnc)(PPh$_3$)], respectively.

With increasing magnetic field, the emission decay time at $T = 1.5$ K becomes shorter. For [Au(dipnc)(PPh$_3$)], the decay time decreases from 130 $\mu$s at $B = 0$ T to 92 $\mu$s at $B = 10$ T. For [Au(dppnc)(PPh$_3$)], the $B$-field induced reduction is even more pronounced. The decay time decreases from 122 $\mu$s ($B = 0$ T) to 57 $\mu$s ($B = 10$ T). Similar effects have already been investigated in detail, for example, for [Ru(bpy)$_3$]$^{2+}$,[25,26] [Ir(ppy)$_3$],[21] and [Ir(btp)$_2$(acac)].[19] Thus, an interpretation of the observed changes is straightforward. At $T = 1.5$ K, the luminescence stems dominantly from the lowest $T_1$ substate I. An external magnetic field induces a mixing of the wave functions of the three $T_1$ substates. Thus, with growing magnetic field, substate I is increasingly perturbed and obtains properties of the substates II and III. Consequently, the probability of the radiative transition from the perturbed substate I(B) to the electronic ground state is enhanced. The observation that the influence of the applied B-field on the emission decay time is stronger for [Au(dppnc)(PPh$_3$)] than for [Au(dipnc)(PPh$_3$)] correlates well with the smaller energy separations between the $T_1$ substates and the shorter decay time of the perturbing substate II of [Au(dppnc)(PPh$_3$)] as compared to [Au(dipnc)(PPh$_3$)]. This behavior is a consequence of the fact that the corresponding energy differences occur in the denominator of the perturbation expressions.[25a,27]

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The observed Zeeman effects demonstrate that for both compounds the emitting state represents a typical triplet state of an organo-transition metal complex.

## 3. Assignments and Concluding Remarks

The analysis of the emission decay behavior of [Au(dipnc)-$(PPh_3)$] and [Au(dppnc)$(PPh_3)$] reveals detailed information about the splitting pattern and the individual decay properties of the three triplet substates, although the emission spectra are very broad and unresolved. In particular, the total zero-field splitting of the emitting $T_1$ state, expressed by the $\Delta E_{\mathrm{I,III}}$ values, has been found to amount to 47 and 29 $cm^{-1}$ for [Au(dipnc)$(PPh_3)$] and [Au(dppnc)$(PPh_3)$], respectively. These values are substantially greater than for triplet states assigned to be largely of ligand centered character. For these latter states, ZFS values of only a few wavenumbers are found.[4a,28,29] On the other hand, the observed ZFS values are much smaller than anticipated for metal centered triplet states of $^3$(5d6p) character. The latter assignment has been suggested, on the basis of DFT calculations,[14,15] for other three-coordinate phosphine gold(I) complexes. The splittings of such a state can be traced back to SOC matrix elements of the type $\langle ^1(\mathrm{dp})|\hat{\mathrm{H}}_{\mathrm{SO}}|^3(\mathrm{d'p})\rangle$, wherein $\hat{\mathrm{H}}_{\mathrm{SO}}$ is the SOC operator, d and d′ are *different* occupied 5d orbitals, and p is the unoccupied 6p orbital (compare ref 28 p 26 and refs 30−32). As, in this situation, the dominating $\hat{\mathrm{H}}_{\mathrm{SO}}$ and the involved orbitals are centered at the metal (one-center integrals[30,31,33]) and as the SOC constant of Au(I) amounts to about 5000 $cm^{-1}$,[34,35] very large ZFSs are expected. Indeed, for metal centered triplet states of third row transition metal compounds, splittings of several hundreds to thousands of $cm^{-1}$ are reported.[36−38] Thus, an assignment of the emitting state as being dominantly of metal centered character ($^3$(5d6p) or $^3$(5d6s6p)) does not seem to correctly describe the lowest triplet states of the studied complexes. Instead, according to the systematics developed for the classification of triplet states of organo-transition metal complexes[4a,28−31] combined with the only moderate values of $\Delta E$(ZFS), it is indicated that significant contributions of phosphine ligand orbitals are involved in the lowest triplet state. In fact, this involvement is not surprising in view of the covalent character found for Au−C bonds[39] and a similar character expected for Au−P bonds. The observed differences between [Au(dipnc)$(PPh_3)$] and [Au(dppnc)$(PPh_3)$] concerning the emission decay rates and values of $T_1$ state splittings are probably caused by modifications of the extent of ligand contributions to the lowest triplet state.

Finally, it is remarked that the strong luminescence of triphosphine gold(I) complexes with high emission quantum yields of up to 75% in combination with an emission decay time of 12 μs at 300 K, as measured for [Au(dipnc)$(PPh_3)$], makes this class of compounds attractive to be used as triplet emitting materials for OLED or sensor applications.

## 4. Experimental Section

[Au(dipnc)$(PPh_3)$] and [Au(dppnc)$(PPh_3)$] were prepared according to refs 16 and 17. Luminescence spectra and emission decay times were measured with complexes dissolved in MTHF ($c \approx 10^{-5}$ mol/L). Samples for quantum yield measurements were prepared by spin-coating dichloromethane solutions of PMMA and a respective complex onto a quartz glass substrate resulting in thin polymer films containing about 1 wt % of the complex. Luminescence spectra at ambient temperature and 77 K were measured with a steady-state fluorescence spectrometer (Horiba Jobin Yvon Fluorolog 3). Experiments at other temperatures were carried out in a He cryostat (Oxford Instruments), in which the He gas flow, He pressure, and heating were controlled. A superconducting magnet, embedded in the He cryostat, was used for high magnetic field measurements. The spectra were recorded with a cooled photomultiplier (RCA C7164R) attached to a double monochromator (SPEX 1404). A pulsed diode laser (PicoQuant $\lambda_{\mathrm{exc}} = 375$ nm) with a pulse width of 100 ps and a nitrogen laser with $\lambda_{\mathrm{exc}} = 337.1$ nm and a pulse duration of 4 ns, respectively, were used as excitation sources for lifetime measurements. Decay times were registered using a FAST ComTec multichannel scaler PCI card with a time resolution of 250 ps. Luminescence quantum yields were measured using a Labsphere (model 4P-GPS-033-SL) integrating sphere with Spectralon inner surface coating.

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