Communication

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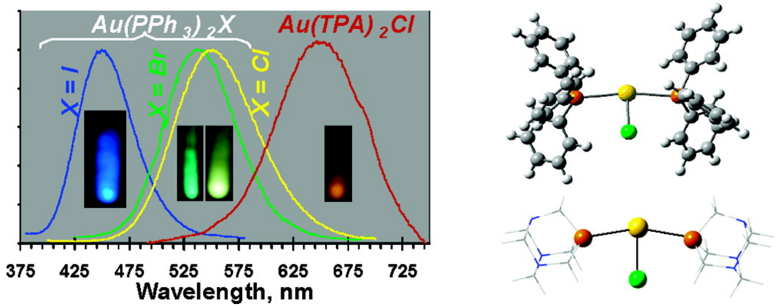

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Phosphorescent metal complexes have led to a quantum leap in the technology of molecular light emitting diodes (MOLEDs) owing to the unity upper limit of the internal electroluminescence quantum efficiency in triplet emitters versus 0.25 for most singlet emitters.[1] While spin−orbit coupling can enhance even organic-centered phosphorescence via a heavy atom effect,[2] metal-centered emissions are particularly favorable because of the direct influence of the metal in making the phosphorescence transitions more allowed and the triplet lifetimes shorter.[3] An attractive class of phosphors that are known to exhibit bright metal-centered emissions is represented by Au(I) complexes.[4] In particular, three-coordinate Au(I) mononuclear and multinuclear complexes exhibit Au-centered phosphorescence with large Stokes' shifts.[5−7] Recent theoretical work suggests that the distortion in the phosphorescent state in *cationic* $Au(PR_3)_3^+$ trigonal complexes is a Jahn−Teller distortion *toward* a T-shape.[8] Hence, we are currently pursuing the idea of whether a systematic variation of the steric bulk in three-coordinate d^{10} complexes will result in an efficient tuning of the phosphorescence energies and lifetimes. The particular complexes examined here are *neutral* $Au(PR_3)_2X$ complexes (X = halide), which should allow for variation of both the halide and phosphine and also for the sublimation of the small molecules into thin films. Despite significant advances made in the area of phosphorescent MOLEDs, efforts by multiple groups continue to fabricate devices with an improved combination of properties that include brightness, charge transport properties, excited-state lifetime, long-term stability, and chromaticity.[1] Stable blue emitters are particularly sought after. We show here that such phosphors can be designed by an intuitive control of the steric bulk in $Au(PR_3)_2X$ complexes.

Quantum mechanical calculations were performed on the full molecular structure of $Au(PPh_3)_2Cl$. A general description of the methodology is given below,[9a] while details are available in the Supporting Information. Figure 1 and Table 1 illustrate the calculated structures for the singlet ground state (S_0) and lowest triplet excited state (T_1). The calculated structures for S_0 are in reasonable agreement with the known crystal structure of $Au(PPh_3)_2Cl$.[10] Method II that includes augmented basis sets[9a] gives better results than the more common treatment in Method I. Figure 1 shows that, upon photoexcitation, the $Au(PPh_3)_2Cl$ molecule distorts *beyond* a T-shape with a γ angle > 180° predicted by both computational methods. In comparison, the corresponding P−Au−P angle in the lowest triplet of $[Au(PPh_3)_3]^+$ was reported as 150.8° in ref 8. The greater distortion in the neutral $Au(PPh_3)_2Cl$ complex is facilitated by the presence of two instead of three bulky phosphines. The calculated excited-state structure also entails elongation of the Au−P bonds without dissociation, while the Au−Cl bond is essentially unchanged.

We have used the theoretical predictions as a guide to examine experimentally whether the luminescence energy can be tuned by varying the steric bulk of the halide and phosphine. The compounds examined here are $Au(PPh_3)_2Cl$, $Au(PPh_3)_2Br$, $Au(PPh_3)_2I$, and $Au(TPA)_2Cl$, where TPA = 1,3,5-triaza-7-phosphaadamantane. The compounds were synthesized following literature procedures[10,11] and characterized by standard analytical methods (see Supporting Information). Figure 2 shows the photoluminescence spectra of the four compounds in the solid state at 77 K. The complexes are also brightly luminescent at room temperature with the emission bands exhibiting thermal broadening. All emission bands have microsecond lifetimes, suggesting phosphorescence, with values increasing

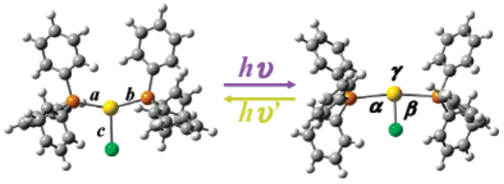

Figure 1. DFT-optimized structures for the S_0 singlet ground state (left) and the T_1 lowest triplet excited state (right) of $Au(PPh_3)_2Cl$.

Table 1. Coordination Geometry of $Au(PPh_3)_2Cl$

method	state	*a*/Å	*b*/Å	*c*/Å	α/deg	β/deg	γ/deg
I	S_0	2.452	2.454	2.673	102.4	103.5	154.1
II	S_0	2.332	2.378	2.538	100.0	116.9	143.2
expt	S_0	2.317	2.336	2.533	109.1	114.8	135.7
I	T_1	2.836	2.843	2.614	83.6	84.7	191.8
II	T_1	2.484	2.486	2.481	89.3	90.2	191.7

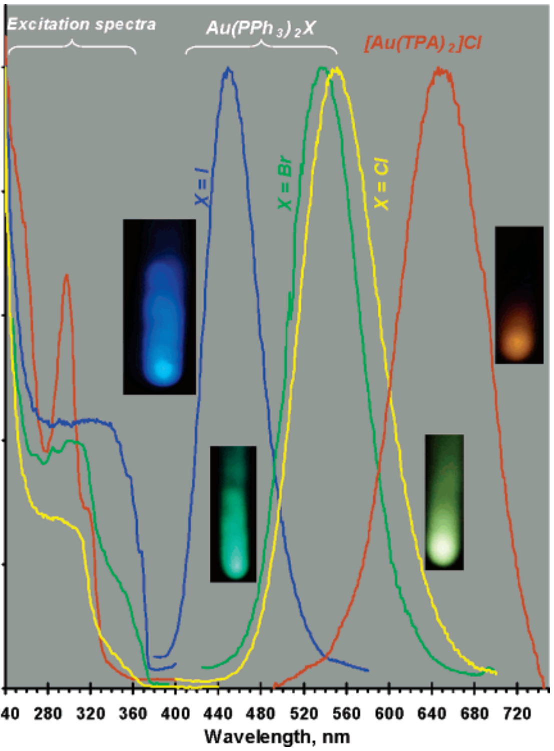

Figure 2. Photoluminescence spectra of $Au(PR_3)_2X$ complexes in the solid state at 77 K.

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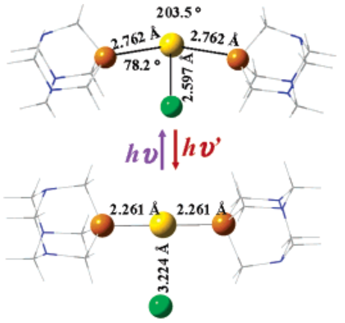

Figure 3. Calculated structure of the T_1 state (top) versus the experimental crystal structure (bottom) of [Au(TPA)$_2$]Cl, suggesting exciplex formation.

upon cooling (τ increased between 19 → 27, 12 → 19, 6.7 → 11, and 9.1 → 18 μs upon cooling Au(PPh$_3$)$_2$Cl, Au(PPh$_3$)$_2$Br, Au(PPh$_3$)$_2$I, and Au(TPA)$_2$Cl, respectively, between 290 → 77 K; errors < 1 μs).

The data illustrate a visible luminescence color change from yellow → green → blue on varying the halide from Cl → Br → I in the Au(PPh$_3$)$_2$X series. The excitation features shown in Figure 2 are significantly red-shifted from the major absorption bands, suggesting direct $S_0 \rightarrow T_1$ excitation, with energies that do not change significantly on ligand variation. These trends are consistent with the distortion beyond a T-shape in the lowest phosphorescent state predicted computationally, as increasing the steric bulk of the halogen is expected to impede such a large molecular motion. As a result, the departure from the ground-state geometry becomes less significant in the luminescent triplet, and consequently, the phosphorescence energy shifts to the blue. In contrast, the decrease in the phosphine cone angle on proceeding from the bulky PPh$_3$ to the unencumbered TPA while keeping the halide constant (Cl) should facilitate the distortion and thus lead to a red shift in the phosphorescence energy. This contention is borne out by the detection of orange phosphorescence in solid Au(TPA)$_2$Cl. However, the reported structure of this compound shows a two-coordinate linear complex and an uncoordinated chloride as a counterion, that is, [Au(TPA)$_2$]Cl.[11] Nevertheless, the chloride is within 3.2 Å of the Au atom and is situated normal to the P−Au−P axis. Such a structure makes [Au(TPA)$_2$]Cl amenable to form an exciplex that bonds the linear complex with the counterion upon photon absorption. This hypothesis is supported by the results of the quantum mechanical/molecular mechanics (QM/MM) calculations[9b] provided in Figure 3, which shows that the crystallographic geometry is rearranged in the lowest triplet excited state to form a structure with a covalent Au−Cl bond, weakened Au−P bonds, and a rather wide P−Au−P γ angle. This beyond-a-T-shape structure is intuitive given the aforementioned computational data for Au(PPh$_3$)$_2$Cl despite the drastic difference in the ground-state coordination.

The experimental and computational data here underscore the significance of the steric factor in the three-coordinate excited state that determines the luminescence energy. The suggested excited-state model explains the lower emission energy of Au(PPh$_3$)$_2$Cl compared to the cationic complex [Au(PPh$_3$)$_3^+$],[6a] as the T_1 state in the former has a greater departure from the S_0 geometry (e.g., in the γ angle; vide supra). This departure results in a large Stokes' shift, computed as 14 272 cm^{-1} for Au(PPh$_3$)$_2$Cl,[12] in good agreement with the spectral data (Figure 2). The [Au(TPA)$_2$]Cl complex was previously reported to be nonluminescent.[6b,c] The orange phosphorescence is rather bright in solid [Au(TPA)$_2$]Cl at both 77 K and room temperature. To our knowledge, this is the first example of a two-coordinate Au(I) complex that is luminescent despite the absence of both Au···Au interactions and aromatic moieties, the presence of which can yield Au-centered and ligand-centered emissions, respectively.[4] However, the compound is two-coordinate only in the ground state, while the observation of luminescence concomitant with the computational data suggests that the chloride becomes a ligand in the excited state, leading to a three-coordinate exciplex. The huge Stokes' shift (~18 000 cm^{-1}) and the rather broad unstructured emission profile are consistent with the dramatic geometrical change in the excited state suggested in Figure 3. Exciplex formation with a counterion is not unique for Au(I) complexes, as a similar explanation was given by Che et al. in dinuclear complexes in which the counterions are often even further from the Au center than the situation here.[13] Likewise, precedents of startling basicity or nucleophilicity upon photoexcitation leading to excited-state ligation are also known, most notably by Gafney et al. for d^6 imine complexes.[14]

In conclusion, the work here illustrates the feasibility of systematic tuning of the emission color by controlling the steric bulk in three-coordinate excited states of Au(I) complexes. MOLED applications are being pursued based on these findings because of desired emission properties that include brightness, stability, and phosphorescence with short triplet lifetimes.

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Supporting Information Available: Detailed descriptions of the experimental and computational methods and data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Review: Yersin, H. *Top. Curr. Chem*. **2004**, *241*, 1.
(2) Recent examples: (a) Omary, M. A.; Kassab, R. M.; Haneline, M. R.; Elbjeirami, O.; Gabbai, F. P. *Inorg. Chem*. **2003**, *42*, 2176. (b) Omary, M. A.; Rawashdeh-Omary, M. A.; Diyabalanage, H. V. K.; Dias, H. V. R. *Inorg. Chem*. **2003**, *42*, 8612. (c) Burress, C.; Elbjeirami, O.; Omary, M. A.; Gabbaï, F. P. *J. Am. Chem. Soc*., published online Aug. 12, 2005 http://dx.doi.org/10.1021/ja053004i.
(3) Long triplet lifetimes lead to brightness saturation due to ground-state depletions. See: Stoffers, C.; Yang, S.; Zhang, F.; Jacobsen, S. M.; Wagner, B. K.; Summers, C. *J. Appl. Phys. Lett*. **1997**, *71*, 1759.
(4) *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M.; Fackler, J. P., Jr., Eds.; Plenum: New York, 1999; Chapter 6.
(5) McCleskey, T. M.; Gray, H. B. *Inorg. Chem*. **1992**, *31*, 1733.
(6) (a) King, C.; Khan, M. N. I.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem*. **1992**, *31*, 3236. (b) Forward, J. M.; Assefa, Z.; Fackler, J. P., Jr. *J. Am. Chem. Soc*. **1995**, *117*, 9103. (c) Assefa, Z.; Forward, J. M.; Grant, T. A.; Staples, R. J.; Hanson, B. E.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2003**, *352*, 31.
(7) (a) Catalano, V. J.; Horner, S. J. *Inorg. Chem*. **2003**, *42*, 8430. (b) Brandys, M.; Puddephatt, R. *J. Am. Chem. Soc*. **2001**, *123*, 4839. (c) Yam, V. W.-W.; Lee, W. K. *J. Chem. Soc., Dalton Trans*. **1993**, 2097. (d) Bojan, V. R.; Fernandez, E. J.; Laguna, A.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Silvestru, C. *J. Am. Chem. Soc*. **2005**, *127*, 11564.
(8) Barakat, K. A.; Cundari, T. R.; Omary, M. A. *J. Am. Chem. Soc*. **2003**, *125*, 14228.
(9) (a) DFT calculations for Au(PPh$_3$)$_2$Cl. Method I: B3LYP/LANL2DZ. Method II: B3PW91/augmented LANL2DZ. (b) QM/MM calculations for Au(TPA)$_2$Cl employed the ONIOM methodology.
(10) Bowmaker, G. A.; Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans*. **1989**, 1089.
(11) Assefa, Z.; Staples, R. J.; Fackler, J. P., Jr. *Acta Crystallogr*. **1996**, *C52*, 305.
(12) Method II data: 344 nm ($S_0 \rightarrow T_1$ absorption), 674 nm ($T_1 \rightarrow S_0$ emission).
(13) Fu, W. F.; Chan, K. C.; Miskowski, V. M.; Che, C. M. *Angew. Chem., Int. Ed*. **1999**, *38*, 2783.
(14) For example: Fan, J.; Helmy, R.; Kassis, A.; Grunseich, A.; Mangubat, P.; Hicks, C.; Stevens, N.; Gafney, H. D. *Inorg. Chem*. **2003**, *42*, 2486.

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