J|A|C|S
COMMUNICATIONS

Golden Metallopolymers with an Active T_1 State via Coordination of Poly(4-vinyl)pyridine to Pentahalophenyl-Gold(I) Precursors

Manal A. Rawashdeh-Omary,*,† José M. López-de-Luzuriaga,*,‡ Maher D. Rashdan,†
Oussama Elbjeirami,† Miguel Monge,‡ María Rodríguez-Castillo,‡ and Antonio Laguna§

Department of Chemistry and Physics, Texas Woman's University, Denton, Texas 76204, Departamento de Química, Universidad de la Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC, Complejo Científico Tecnológico, 26006 Logroño, Spain, and Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Received December 9, 2008; E-mail: momary@twu.edu; josemaria.lopez@unirioja.es

Introduction of metal centers to organic polymers can attain phosphorescent metallopolymers with desirable properties for a variety of photonic applications. For example, the lowest-triplet (T_1) state of organic polymers represents a dark state that reduces the efficiency of polymer light-emitting diodes (PLEDs) upon doping a phosphorescent molecule. This problem is particularly severe for conjugated polymers used as PLED hosts for blue or green phosphors because the host T_1 state is usually lower in energy, leading to reverse energy transfer that depopulates the desired dopant emission levels.[1] One possible amelioration is to utilize nonconjugated polymers with high-energy T_1 states, such as the carbazole derivatives described by Brunner et al., the use of which as host has resulted in significant performance enhancement for green phosphorescent PLEDs vs those based on commercially available hosts (e.g., poly(*N*-vinylcarbazole), PVK).[2] A promising alternative approach is to synthesize brightly phosphorescent metallopolymers because such materials will have an active T_1 state that may be harnessed directly, eliminating the need to dope an external guest phosphor. This concept has been verified recently using synthetic polymers that are capable of coordinating to certain transition metals or lanthanides, such as the Pt(II) metallopolymers reported by Thompson, Frechet and co-workers[3] and the Eu(III) metallopolymers reported recently by Holliday and co-workers.[4] Here we show an expansion of this concept to Au-based metallopolymers synthesized from *commercially available polymers that can coordinate to Au(I) precursors*. The spectroscopic and material properties of this new class of metallopolymers are evaluated toward utilization in PLEDs. This investigation also provides further manifestation of interesting chemistry and photophysics that can be exhibited by *N*-heterocyclic coordination compounds of Au(I) despite the perceived incompatibility of the soft Au and hard N centers.[5,6] Thus, the work herein expands this chemistry from small molecules to metallopolymers of Au(I) in a manner akin to that established for the harder Pt(II) ion.[3,7]

Metallopolymers $[Au(C_6F_5)PVP]$ (**1**) and $[Au(C_6Cl_5)PVP]$ (**2**) (PVP = poly(4-vinylpyridine)) were prepared by reaction of the corresponding Au(I) precursors $[Au(C_6X_5)THT]$ (X = F or Cl; THT = tetrahydrothiophene) with PVP (MW = 60 000 as obtained from Aldrich) in dichloromethane at room temperature, using a 1:1 Au/PVP molar ratio. The reaction occurs instantly and is clearly evidenced by the appearance of a rather bright green luminescence for the product upon mixing the nonluminescent starting materials (Figure 1, top). The Au content in the metallopolymers was determined via gravimetric analysis. Thus, chemical reduction of metallopolymers **1** and **2** with hydrazine followed by calcination of the organic residue at 700 °C led to products with 35.5% (**1**) and 29.8% (**2**) Au in weight content, corresponding to 84% (**1**) and 83% (**2**) occupation of pyridine positions. The reactions can be monitored by the in situ addition of the Au(I) precursor to a PVP solution in d_6-DMSO, suggesting successive coordination of the polymer pyridine units to $[Au(C_6X_5)]$ moieties as illustrated in Figure 1 (bottom) for the reaction with X = F. When the Au/PVP molar ratio is 1:1, the signals of free pyridine fragments persist, albeit at rather low intensity, consistent with the aforementioned high Au content in **1**.

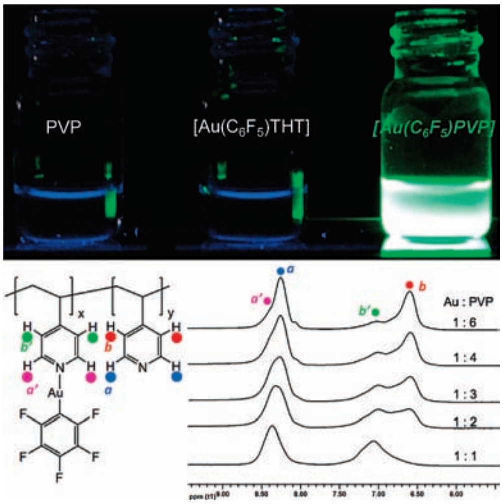

Figure 1. Top: Illustration of the formation of the phosphorescent metallopolymer **1** from nonluminescent starting materials; pictures are taken for solutions under 365 nm irradiation from a hand-held mercury lamp. Bottom: ^1H NMR spectra of the in situ reaction of $[Au(C_6F_5)THT]$ and PVP vs molar ratio in d_6-DMSO.

Both **1** and **2** exhibit bright photoluminescence (PL) in the solid state. Temperature-dependent PL and PL excitation (PLE) spectra and lifetimes are shown in Figure 2. These data reveal remarkable sensitivity of the luminescence energies, intensities, and lifetimes to both excitation wavelength and temperature. For **1**, the emission can be fine-tuned between four emission maxima by varying λ_{exc} even at the same temperature. The most striking result for **2**, on the other hand, is coarse tuning from blue at 77 K to yellow at RT, manifesting luminescence thermochromism. Unstructured emissions with microsecond lifetimes are obtained in all cases (Figure 2), consistent with metal-centered phosphorescence. PL quantum yields at room temperature (Φ_{RT}), measured in an integrating sphere for packed powder samples, are 0.63 and 0.28 for neat solids of **1** and

---

[†] Texas Woman's University.
[‡] Universidad de la Rioja.
[§] Universidad de Zaragoza-CSIC.

10.1021/ja809585n CCC: $40.75

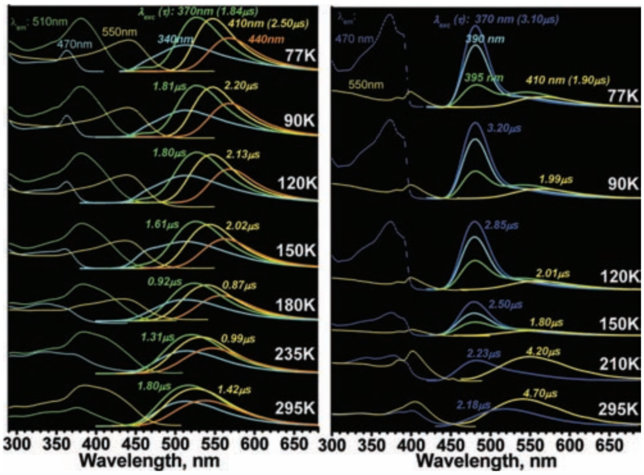

Figure 2. Temperature-dependent PL (solid curves) and PLE (dashed curves) spectra and lifetimes of solid metallopolymers **1** (left) and **2** (right). Intensities are not normalized, but baselines are offset for clarity.

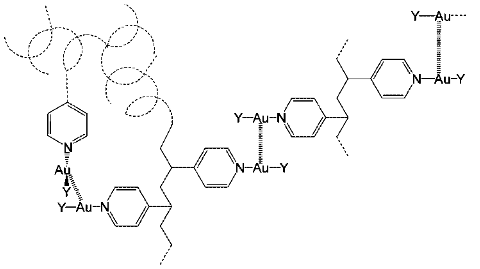

Figure 3. Suggested structural model showing intrachain and interchain aurophilic interactions in metallopolymers **1** and **2**.

2, respectively, using $\lambda_{exc} = 410$ nm. Consistent with the higher Φ_{RT} values for **1** is the only small increase in the PL intensities and phosphorescence lifetimes upon cooling to cryogenic temperatures (Figure 2), suggesting a small value for the nonradiative decay rate constant (k_{nr}). Further details about the photophysical parameters (Φ, k_r, k_{nr}, τ) vs temperature and excitation for **1** and **2** are in the Supporting Information.

Given that the complexes are two-coordinate (Figure 1), their emissions are related to aurophilic Au(I)···Au(I) interactions, following literature conventions for Au(I) complexes.[8] These interactions can be both intra- and interchain in the metallopolymers (Figure 3). One would expect multiple sites that differ in Au(I)···Au(I) distance, number of next-neighbor Au(I) atoms, geometry, etc., and that the distribution of these sites to be temperature and excitation dependent, giving rise to corresponding shifts in the emission maxima. This is substantiated by the spectral data in Figure 2, quite drastically in some instances (e.g., see the qualitative emission color change upon varying λ_{exc} for **1** at 77 K and for **2** at 210 K). Similar observations have been reported in the small molecule regime for Au(I) linear complexes in rigid solutions and/or doped solids.[9] The electronic transitions in the analogous small molecular complexes [Au(C_6Cl_5)(Py)] have been assigned as ligand−metal (C_6Cl_5−Au) to ligand (Py) charge transfer.[5] We adopt this assignment for the excitation bands of metallopolymers **1** and **2**, whereas we assign their phosphorescence bands to Au−Au bonded excimeric triplet states of different aggregated species. Time-resolved measurements revealed no risetimes in the ns or μs time scale, suggesting preassociation of complexes prior to photoexcitation, as known for both organic[10a] and inorganic[9,10b] excimers in rigid media. Varying the Au loading in solution within the solubility limit results in luminescence intensity changes; see Figure S1.

Finally, we assess the suitability of the new metallopolymers for potential PLED applications:[1−3,11] (a) High solid-state Φ_{RT} values are desired to inhibit concentration quenching; the 0.63 and 0.28 values for **1** and **2**, respectively, are rather high for solid molecular materials without doping.[12] (b) High-energy triplet excitons are desired to be harvested and/or transferred to other visible emitters; this is satisfied due to the green most active T_1 excitons in **1** and **2**, providing suitable energy levels for exothermic and endothermic energy transfer to red and blue color centers, respectively. (c) Short triplet lifetimes (μs instead of ms) to inhibit triplet−triplet annihilation and allow rapid on/off switching. (d) Long excitation wavelengths to warrant low turn-on voltage and overlap with the host PL profile if doping is needed. Excitations extending to $\lambda > 400$ nm (Figure 2) are indeed longer than those for the typical PLED host PVK. (e) Air, light, moisture, and thermal stability are required, which is true for both **1** and **2**. (f) Charge neutrality is desirable to prevent leakage of electrons or holes to the electrodes; the metallopolymers herein are neutral complexes. (g) High solubility is required for thin-film processing from solution. Although the starting materials are highly soluble, the final metallopolymer products herein do not exhibit high enough solubility in common organic solvents to allow spin coating of neat material into thin films. Strategies to circumvent this limitation by multiple chemical and physical means will be investigated, for example, by introducing alkyl substituents to the polymer or Y ligand and/or preparing submolar blends. With these overall favorable properties, efforts will be pursued to evaluate the performance of this class of Au(I) metallopolymers and analogues thereof as PLED phosphors.

Acknowledgment. M.A.R.-O. acknowledges the Defense Advanced Research Program Agency (DARPA) for supporting this project through Young Investigator Award W71B7J-7078-B368. The Spanish team acknowledges support for DGI (MEC)/FEDER (CTQ2007-67273-C02-02) and CAR grants.

Supporting Information Available: Further synthetic and spectral details for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Sudhakar, M.; Djurovich, P. I.; Hogen-Esch, T. E.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7796.

(2) van Dijken, A.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W.; Rothe, C.; Monkman, A.; Bach, I.; Stössel, P.; Brunner, K. *J. Am. Chem. Soc.* **2004**, *126*, 7718.

(3) Furuta, P. T.; Deng, L.; Garon, S.; Thompson, M. E.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15388.

(4) Chen, X.-Y.; Yang, X.; Holliday, B. J. *J. Am. Chem. Soc.* **2008**, *130*, 1546.

(5) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E.; Pérez, J.; Rodríguez-Castillo, M. *Gold Bull.* **2007**, *40*, 172.

(6) (a) Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R.; Diyabalanage, H, V. K.; Palehepitiya; Gamage, C. S.; Dias, H. V. R. *Inorg. Chem.* **2005**, *44*, 8200. (b) Omary, M. A.; Mohamed, A. A.; Rawashdeh-Omary, M. A.; Fackler, J. P., Jr. *Coord. Chem. Rev.* **2005**, *249*, 1372. (c) Mohamed, A. A.; Abdou, H. E.; Irwin, M. D.; López-de-Luzuriaga, J. M.; Fackler, J. P., Jr. *J. Cluster. Sci.* **2005**, *44*, 8200. (d) Yang, C.; Messerschmidt, M.; Coppens, C.; Omary, M. A. *Inorg. Chem.* **2006**, *45*, 6592.

(7) Kwok, C.-C.; Yu, S.-C.; Sham, I. H. T.; Che, C.-M. *Chem. Commun.* **2004**, 2512.

(8) Roundhill, D. M.; Fackler, J. P., Jr. *Optoelectronic Properties of Inorganic Compounds*; Plenum: New York, 1999; Chapter 6.

(9) (a) White-Morris, R. L.; Olmstead, M. M.; Jiang, F.; Tinti, D. S.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 2327. (b) Rawashdeh-Omary, M A.; Omary, M. A.; Patterson, H. H.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 11237. (c) Hettiarachchi, S. R.; Rawashdeh-Omary, M. A.; Kanan, S. M.; Omary, M. A.; Patterson, H. H.; Tripp, C. P. *J. Phys. Chem. B* **2002**, *106*, 10058. (d) Elbjeirami, O.; Yockel, S.; Campana, C. F.; Wilson, A. K.; Omary, M. A. *Organometallics* **2007**, *26*, 2550.

(10) (a) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587. (b) Omary, M. A.; Patterson, H. H. *J. Am. Chem. Soc.* **1998**, *120*, 7696.

(11) Review: Yersin, H. *Top. Curr. Chem.* **2004**, *241*, 1.

(12) Zhao, S.-B.; McCormick, T.; Wang, S. *Inorg. Chem.* **2007**, *46*, 10965.

JA809585N