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# Metallophilic Interactions in Closed-Shell Metal-Metal Bonded Luminescent Systems and Their Tunability for Excited State Energy Transfer

Howard H. Patterson

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**Final Report for Period:** 08/2007 - 07/2008**Submitted on:** 04/03/2009**Principal Investigator:** Patterson, Howard H.**Award ID:** 0315877**Organization:** University of Maine**Submitted By:**

Patterson, Howard - Principal Investigator

**Title:**

Metallophilic Interactions in Closed-Shell Metal-Metal Bonded Luminescent Systems and Their Tunability for Excited State Energy Transfer

### Project Participants

#### Senior Personnel

**Name:** Patterson, Howard**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Howard Patterson supervised the team of students working on this project, undergraduates, graduate students and post-doctoral research associates in the area of physical inorganic chemistry with emphasis of training on development of new nanosystems.

#### Post-doc

**Name:** Lu, Haiyan**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Haiyan Lu was a postdoc working on optical memory of the different mixed metal systems. Now he is an Associate Professor of Chemistry at Jilin University in China.

**Name:** Yson, Renante**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Renante Yson was a postdoc working on the synthesis, photochemical and photophysical properties of the different mixed metal systems. Now he is a research computing system administrator in the department of Chemistry at the University of Nevada, Reno, Nevada.

#### Graduate Student

**Name:** Guo, Zhonghua**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Zhonghua Guo, a Ph.D. student, has carried out studies of tunable energy transfer with d10-d10 exciplexes as donor ions and lanthanide ions as acceptors.

**Name:** Li, Xiaobo**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Xiaobo Li is a graduate student working on the project but has not been directly supported by it. He is supported by University/Departmental funding.

**Name:** Gomez, Robert**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Robert Gomez carried out Raman studies on nanosystems of d8 or d10 ions doped in alkali halides.

**Name:** Palla, Velladri**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Veladri Palla was a graduate student working on the project but was not directly supported by it. He was supported by University/Departmental funding. He has completed his M.S. thesis and received his degree in May of 2007. His M.S. thesis is titled 'Heterometallic Interactions of d8-d10 Metal Ions in the Presence of +2 Cations'.

**Name:** Colis, Julie

**Worked for more than 160 Hours:** Yes

**Contribution to Project:**

Julie Colis has completed her Ph.D. thesis and received her degree in May of 2004. Her Ph.D. thesis is titled 'Energy Transfer and Optical Memory Studies of d10 Closed Shell Homo and Heterometallic Dicyanide Systems'.

**Name:** Schaefer, Brian

**Worked for more than 160 Hours:** Yes

**Contribution to Project:**

Brian Schaefer has completed his M.S. thesis and received his degree in May of 2006. His M.S. thesis is titled 'A Study of the Heterometallic d10 Interaction and the Effect of Light and Solvent on Silver Doped Faujasite'.

### Undergraduate Student

**Name:** Nicholas, Aaron

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Aaron Nicholas carried out luminescence energy transfer crystal studies of d8 and d10 donor ions with Eu<sup>3+</sup>, Tb<sup>3+</sup> and Lanthanide acceptor ions.

**Name:** Welch, David

**Worked for more than 160 Hours:** No

**Contribution to Project:**

David Welch did molecular simulation studies to model d8 and d10 clusters in alkali halides. He has completed his Bachelor thesis and received his degree in May of 2008. His Bachelor thesis is titled 'Computational Chemistry of Metal Dicyanide Nanoclusters within Alkali Halide Lattices'.

**Name:** Look, Kendra

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Kendra Look carried out luminescence energy crystal studies of d8 donor ions with Eu<sup>3+</sup> and Tb<sup>3+</sup> acceptor ions.

**Name:** Bolton, Jason

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Jason has completed a series of experiments to characterize the metal-metal interaction of K<sub>2</sub>Pt(CN)<sub>4</sub> with KAu(CN)<sub>2</sub> and KAg(CN)<sub>2</sub> in solution at various concentrations.

**Name:** Clay, Michael

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Michael has completed a series of experiments to characterize the metal-metal interaction of K<sub>2</sub>Pt(CN)<sub>4</sub> with KAu(CN)<sub>2</sub> and KAg(CN)<sub>2</sub> in solution at various concentrations.

**Name:** Richards, Chris

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Chris Richards has completed a senior undergraduate thesis titled Optical Memory Studies of [Ag(CN)<sub>2</sub>]- Doped in Sodium Chloride Single Crystals in May, 2005.

**Name:** Wyman, Jodi

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Jodi has completed a series of experiments to characterize the metal-metal interaction of  $K_2Pt(CN)_4$  with  $KAu(CN)_2$  and  $KAg(CN)_2$  in solution at various concentrations.

### Technician, Programmer

### Other Participant

### Research Experience for Undergraduates

### Organizational Partners

#### Harvard University

Crystallography of  $La[Ag_xAu_{1-x}(CN)_2]_3$  and  $Eu[Ag_xAu_{1-x}(CN)_2]_3$  ( $x = 0-1$ ) were determined by Richard Staples at the Department of Chemistry and Chemical Biology, Harvard University. The collaborative research was carried out and two papers were published. These two publications are 'Metallophilic Interactions in Closed-Shell d10 Metal-Metal Dicyanide Bonded Luminescent Systems  $Eu[Ag_xAu_{1-x}(CN)_2]_3$  and Their Tunability for Excited State Energy Transfer' by Colis, JCF; Staples, R; Tripp, C; Labrecque, D; Patterson, H in Journal of Physical Chemistry B, volume 109, 2005, page 102 and 'Observation of a mixed metal transition in heterobimetallic Au/Ag dicyanide systems' by Hettiarachchi, SR; Schaefer, BK; Yson, RL; Staples, RJ; Herbst-Irmer, R; Patterson, HH, in Inorganic Chemistry, volume 46, 2007, page 6997.

#### University of Southern Maine

The collaborative research was carried out with James Ford, Henry J. Tracy, Alora B. Carrier, Aaron Keller. One paper was published by Lu, H; Yson, R; Ford, J; Tracy, HJ; Carrier, AB; Keller, A; Mullin, JL; Poissan, MJ; Sawan, S; Patterson, HH with the title 'Tunable energy transfer from d10 heterobimetallic dicyanide(I) donor ions to terbium(III) acceptor ions in luminescent  $Tb[Ag_xAu_{1-x}(CN)_2]_3$  ( $x=0 \rightarrow 1$ )' in Chemical Physics Letters, volume 443, 2007, page 55.

#### University of New England

The collaborative research was carried out with Jerome L. Mullin, Michelle J. Poissan, Samuel Sawan. One paper was published by Lu, H; Yson, R; Ford, J; Tracy, HJ; Carrier, AB; Keller, A; Mullin, JL; Poissan, MJ; Sawan, S; Patterson, HH with the title 'Tunable energy transfer from d10 heterobimetallic dicyanide(I) donor ions to terbium(III) acceptor ions in luminescent  $Tb[Ag_xAu_{1-x}(CN)_2]_3$  ( $x=0 \rightarrow 1$ )' in Chemical Physics Letters, volume 443, 2007, page 55.

#### University of North Texas

The collaborative research was carried out with Professor Omary, who was former student in my group. Two papers were published with the title 'Optical memory and multistep luminescence thermochromism in single crystals of  $K_2Na[Ag(CN)_2]_3$ ' by Omary, MA; Colis, JCF; Larochelle, CL; Patterson, HH, in Inorganic Chemistry, volume 46, 2007, page 3798 and 'Photophysics of bis(thiocyanato)gold(I) complexes: Intriguing structure-luminescence relationships' by Arvapally, RK; Sinha, P; Hettiarachchi, SR; Coker, NL; Bedel, CE; Patterson, HH; Elder, RC; Wilson, AK; Omary, MA in Journal of Physical Chemistry C, volume 111, 2007, page 10689.

#### Simon Fraser University

The collaborative research was carried out with Professor Leznoff. and one paper was published with the title 'Structural and spectroscopic impact of tuning the stereochemical activity of the lone pair in lead(II) cyanoaurate coordination polymers via ancillary ligands' by Katz, MJ; Michaelis, VK; Aguiar, PM; Yson, R; Lu, H; Kaluarachchi, H; Batchelor, RJ; Schreckenbach, G; Kroeker, S; Patterson, HH; Leznoff, DB in Inorganic Chemistry, volume 47, 2008, page 6353.

#### University of Göttingen

The collaborative research was carried out with Doctor Regine Herbst-Irmer and one paper was published with the title 'Observation of a mixed metal transition in heterobimetallic Au/Ag dicyanide systems' by Hettiarachchi, SR; Schaefer, BK; Yson, RL; Staples, RJ; Herbst-Irmer, R; Patterson, HH, in Inorganic Chemistry, volume 46, 2007, page 6997.

#### Franklin and Marshall College

The collaborative research was carried out with Professor Larochelle, who was a former student in my group. Two papers were published with the title 'Optical memory and multistep luminescence thermochromism in single crystals of  $K_2Na[Ag(CN)_2]_3$ ' by Omary, MA; Colis, JCF;

Larochelle, CL; Patterson, HH, in *Inorganic Chemistry*, volume 46, 2007, page 3798 and 'Tunable Photoluminescence Studies of Closed-shell Heterobimetallic Au-Ag Dicyanide Layered Systems' by Colis, JCF; Larochelle, C; Fernandez, EJ; Lopez-De-Luzuriaga, JM; Monge, M; Laguna, A; Tripp, C; Patterson, H in *Journal of Physical Chemistry B*, volume 109, 2005, page 4317.

### Other Collaborators or Contacts

Ab initio molecular modeling of the mixed metal systems  $\text{La}[\text{AuxAg}_{1-x}(\text{CN})_2]_3$  ( $x=0-1$ ) have been carried out with the objective of comparing the bonding in the pure systems with the mixed metal systems by Fernandez, E. J.; Lopez-de-Luzuriaga, J. M.; and Monge, M. from the University of Rioja, Spain. For example, the mixed metal systems have strong luminescence at room temperature while the pure systems have weak luminescence. The MO models provide an explanation for these experimental results. The ab initio molecular modeling is currently being extended to the corresponding  $\text{Eu}^{3+}$  systems in order to microscopically describe energy transfer processes in the pure versus mixed Au, Ag systems.

### Activities and Findings

#### **Research and Education Activities: (See PDF version submitted by PI at the end of the report)**

Activities and findings are integrated. See the attached file

#### **Findings:**

Activities and findings are integrated. See the attached file

#### **Training and Development:**

Julie Colis has completed her Ph.D. in Chemistry in May of 2004 and has become proficient at cryogenics, luminescence, Raman spectroscopy, and interpretation of computational chemistry and X-ray crystallography.

Brian Schaefer has completed his M.S. in Chemistry in May of 2006. He has become proficient in the use of cryogenics, luminescence, and Raman spectroscopy.

Velladri Palla has completed his M.S. in Chemistry in May of 2007. He has become proficient in the use of cryogenics and luminescence.

#### **Outreach Activities:**

### Journal Publications

Katz, MJ; Michaelis, VK; Aguiar, PM; Yson, R; Lu, H; Kaluarachchi, H; Batchelor, RJ; Schreckenbach, G; Kroeker, S; Patterson, HH; Leznoff, DB, "Structural and spectroscopic impact of tuning the stereochemical activity of the lone pair in lead(II) cyanoaurate coordination polymers via ancillary ligands", *INORGANIC CHEMISTRY*, p. 6353, vol. 47, (2008). Published, 10.1021/ic800425

Colis, JCF; Staples, R; Tripp, C; Labrecque, D; Patterson, H, "Metallophilic interactions in closed-shell d(10) metal-metal dicyanide bonded luminescent systems  $\text{Eu}[\text{AgxAu}_{1-x}(\text{CN})_2]_3$  and their tunability for excited state energy transfer", *JOURNAL OF PHYSICAL CHEMISTRY B*, p. 102, vol. 109, (2005). Published, 10.1021/jp046717

Hettiarachchi, SR; Schaefer, BK; Yson, RL; Staples, RJ; Herbst-Irmer, R; Patterson, HH, "Observation of a mixed-metal transition in heterobimetallic Au/Ag dicyanide systems", *INORGANIC CHEMISTRY*, p. 6997, vol. 46, (2007). Published, 10.1021/ic700780

Lu, H; Yson, R; Ford, J; Tracy, HJ; Carrier, AB; Keller, A; Mullin, JL; Poissan, MJ; Sawan, S; Patterson, HH, "Tunable energy transfer from d(10) heterobimetallic dicyanide(I) donor ions to terbium(III) acceptor ions in luminescent  $\text{Tb}[\text{AgxAu}_{1-x}(\text{CN})_2]_3$  ( $x=0 \rightarrow 1$ )", *CHEMICAL PHYSICS LETTERS*, p. 55, vol. 443, (2007). Published, 10.1016/j.cplett.2007.06.01

Guo, ZH; Yson, RL; Patterson, HH, "Solvent dependent tunable energy transfer d(10) metal dicyanide nanoclusters with  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  of rare earth ions", *CHEMICAL PHYSICS LETTERS*, p. 340, vol. 445, (2007). Published, 10.1016/j.cplett.2007.07.07

Arvapally, RK; Sinha, P; Hettiarachchi, SR; Coker, NL; Bedel, CE; Patterson, HH; Elder, RC; Wilson, AK; Omary, MA, "Photophysics of bis(thiocyanato)gold(I) complexes: Intriguing structure-luminescence relationships", JOURNAL OF PHYSICAL CHEMISTRY C, p. 10689, vol. 111, (2007). Published, 10.1021/jp071935

Omary, MA; Colis, JCF; Larochelle, CL; Patterson, HH, "Optical memory and multistep luminescence thermochromism in single crystals of  $K_2Na[Ag(CN)_2]_3$ ", INORGANIC CHEMISTRY, p. 3798, vol. 46, (2007). Published, 10.1021/ic070198

Guo, ZH; Yson, RL; Patterson, HH, "Tunable energy transfer between  $[Au(CN)_2]^{-(n)}$  luminescent nanoclusters and rare earth ions in aqueous solution", CHEMICAL PHYSICS LETTERS, p. 373, vol. 433, (2007). Published, 10.1016/j.cplett.2006.11.01

Colis, JCF; Larochelle, C; Fernandez, EJ; Lopez-De-Luzuriaga, JM; Monge, M; Laguna, A; Tripp, C; Patterson, H, "Tunable photoluminescence of closed-shell heterobimetallic Au-Ag dicyanide layered systems", JOURNAL OF PHYSICAL CHEMISTRY B, p. 4317, vol. 109, (2005). Published, 10.1021/jp045868

Colis, JCF; Larochelle, C; Staples, R; Herbst-Irmer, R; Patterson, H, "Structural studies of lanthanide ion complexes of pure gold, pure silver and mixed metal (gold silver) dicyanides", DALTON TRANSACTIONS, p. 675, vol. , (2005). Published, 10.1039/b413967

### **Books or Other One-time Publications**

#### **Web/Internet Site**

#### **Other Specific Products**

#### **Contributions**

##### **Contributions within Discipline:**

A paper was presented by H. H. Patterson at 227th American Chemical Society National Meeting in Anaheim, California in the Nanoscience Session. The title was 'Tunable luminescence and optical memory in nanoclusters of  $Ag(CN)_2^-$  and  $Au(CN)_2^-$  doped in alkali halide matrices' and was co-authored by M. A. Omary, J. C. F. Colis and S. R. Hettiarachchi. Omary and Hettiarachchi are former Ph.D. students of Patterson who are now faculty at the University of North Texas and University of Ruhuna, respectfully.

'Luminescence Energy Tunability and Enhanced Luminescence Intensity for Closed Shell d10 Heterobimetallic Gold-Cyanide Systems' Symposium on Frontiers in Inorganic Spectroscopy and Photochemistry . 229th American Chemistry Society National Meeting, San Diego, California. March 2005, H.H. Patterson, J.C. Colis, Z. Guo.

'Silver clusters doped in zeolites as photocatalysts for the decomposition of NO<sub>x</sub>, Malathion, Carbaryl and other pollutants' Symposium of Environmental Applications of Inorganic Chemistry Advanced Catalysis. 229th American Chemistry Society National Meeting, San Diego, California. March 2005, B. Schaefer; H.H. Patterson.

'Oligomerization, Exciplex Tuning, and Energy Transfer in Dicyano Complexes of Ag(I) and Au(I)' Symposium on the Metal-Cyanide Renaissance, Tricentennial of the Synthesis of Prussian Blue, 229th American Chemistry Society National Meeting, San Diego, California. March 2005, H.H. Patterson, J.C. Colis, Z. Guo.

'Optical memory of single crystals of dicyanoargentate(I)' 230th ACS National Meeting, Washington, D.C., August 28-Sept. 1, 2005. H. H. Patterson,; J. C. Colis ; C. Richards; M. A. Omary.

'Excited state energy transfer in d10-d8 mixed-metal donor systems with rare earth acceptor ions' Chemistry of Lanthanides and Actinides. 234th ACS National Meeting, Boston, MA, August 19-23, 2007, R. Yson; H. Lu; A. Nicholas; H. Patterson.

'Photocatalytic activity of zeolite-supported Ag and AgFe nanoclusters' Inorganic Catalysis. 234th ACS National Meeting, Boston, MA, August 19-23, 2007, R. Gomez; H. Lu; R. Yson; H. Patterson.

'Optical memory application for nanoclusters of dicyanocuprate(I) ions doped in alkali halide crystals' Nanoscience: Applications. 234th ACS National Meeting, Boston, MA, August 19-23, 2007, H. Lu; X. Li; R. Yson; R. Gomez; H. Patterson.

'Temperature-dependent optical memory for dicyano Ag(I) complexes', Spectroscopy of Inorganic Systems. 234th ACS National Meeting, Boston, MA, August 19-23, 2007, H. Lu; S. Hurley; X. Li; M. A. Rawashdeh-Omary; H. H. Patterson; M. A. Omary.

'Solvent dependent tunable energy transfer between d10 metal dicyanide nanoclusters and Eu<sup>3+</sup> and Tb<sup>3+</sup> rare earth ions' Chemistry of Lanthanides and Actinides. 234th ACS National Meeting, Boston, MA, United States, August 19-23, 2007, Z. Guo; H. H. Patterson.

#### **Contributions to Other Disciplines:**

#### **Contributions to Human Resource Development:**

In this project, undergraduate science majors as well as graduate students have been involved as participants in the research activities. Seven undergraduates and six graduate students carry out research in our group. Each student has been provided technical training in chemical synthesis, luminescence spectroscopy, vibrational spectroscopy, and computer modeling-techniques that are important in nanoscale science and engineering. Two graduate students Julie Colis and Brian Schaefer directly supported by this grant have graduated with a Ph.D and Masters degree.

#### **Contributions to Resources for Research and Education:**

#### **Contributions Beyond Science and Engineering:**

#### **Categories for which nothing is reported:**

Activities and Findings: Any Outreach Activities

Any Book

Any Web/Internet Site

Any Product

Contributions: To Any Other Disciplines

Contributions: To Any Resources for Research and Education

Contributions: To Any Beyond Science and Engineering

1. Omary, M. A.<sup>†</sup>; Colis, J. C. F.<sup>\*</sup>; Larochelle, C. L.<sup>‡</sup>; Patterson, H. H.<sup>\*</sup> Optical memory and multistep luminescence thermochromism in single crystals of  $K_2Na[Ag(CN)_2]_3$ . *Inorg. Chem.* **2007**, *46*, 3798.

<sup>\*</sup>Department of Chemistry, University of Maine, Orono, Maine 04469; <sup>‡</sup>Department of Physics, Franklin and Marshall College, Lancaster, PA 17604; <sup>†</sup>Department of Chemistry, University of North Texas, Denton, Texas 76203.

**Summary:** Single crystals of the layered compound  $K_2Na[Ag(CN)_2]_3$  exhibit a dual emission with high-energy (HE) and low-energy (LE) phosphorescence bands at 313 and 402 nm, respectively. Remarkably, the crystals exhibit "optical memory," in which a new emission band with intermediate energy (IE) at 380 nm is generated upon laser irradiation ( $\lambda_{ex}=266$  nm) at cryogenic temperatures. The irradiated crystals reinstate their original luminescence spectrum upon heating to room temperature and then recooling. In addition to these unusual "write/read/erase" changes, the crystals also exhibit multistep luminescence thermochromism such that the LE/HE intensity ratio increases between 17 and 80 K but then decreases upon further heating. The unprecedented occurrence of

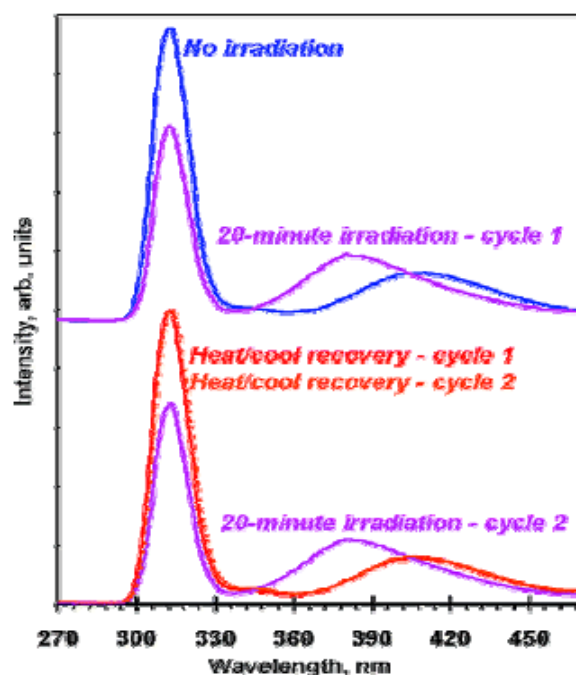


Figure 1 Luminescence spectra of  $K_2Na[Ag(CN)_2]_3$  single crystals at 70 K before and after irradiation with 266 nm laser light. The results of a repetition of the same experiment are shown after the same sample was heated to room temperature and then cooled again to 70 K in the dark.

both novel phenomena in one compound has been related to reversible photophysical changes instead of irreversible photochemical changes. These phenomena (optical memory and luminescence thermochromism) occur reversibly in pure (undoped) crystals of one compound, having potential applications in data storage and temperature sensing.



2. Guo, Z.; Yson, R. L.; Patterson, H. H. Tunable energy transfer between luminescent nanoclusters and rare earth ions in aqueous solution. *Chem. Phys. Lett.* **2007**, 433, 373.

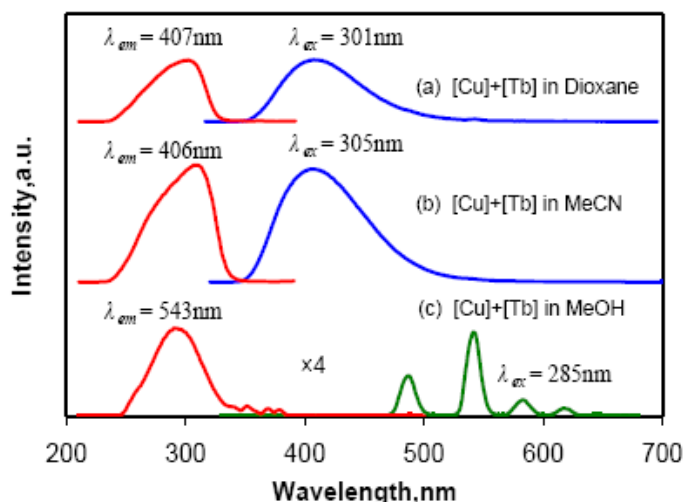
*Department of Chemistry, University of Maine, Orono, Maine 04469.*

**Summary:** Energy transfer has been studied between dicyanoaurate(I) luminescent nanocluster donor ions and Tb<sup>3+</sup> and Eu<sup>3+</sup> acceptor ions in aqueous solutions using steady-state luminescence at room temperature. It was found that the f–f transition emission intensities of Tb<sup>3+</sup> ions can be sensitized and enhanced by varying the dicyanoaurate(I) donor ion's concentration, due to the formation of different excimer and exciplex nanoclusters. However, the f–f transition emission intensities of Eu<sup>3+</sup> ions are not enhanced but the donor's emission is quenched through a non-radiative charge transfer pathway. The Stern–Völmer constants showed different quenching efficiencies for different nanoclusters of the donor.

3. Guo, Z.; Yson, R. L.; Patterson, H. H. Solvent dependent tunable energy transfer of d<sup>10</sup> metal dicyanide nanoclusters with Eu<sup>3+</sup> and Tb<sup>3+</sup> rare earth ions. *Chem. Phys. Lett.* **2007**, 445, 340.

*Department of Chemistry, University of Maine, Orono, Maine 04469.*

**Summary:** The luminescence energy and intensity of d<sup>10</sup> copper(I), silver(I), and gold(I) dicyanide nanoclusters has been found to exhibit high tunability as energy transfer donors in different organic solvents. For Tb<sup>3+</sup> acceptor ions, the energy transfer efficiency, which is proportional to the spectral overlap extent between the donor emission and the acceptor absorption, depends on the solvent tunability of the donor emission energy. For Eu<sup>3+</sup> acceptor ions, energy



*Figure 2 Energy transfer of Cu(CN)<sup>2-</sup> clusters with Tb<sup>3+</sup> acceptor ions in acetonitrile or dioxane exhibits no energy transfer while in methanol energy transfer is observed.*

transfer can be “tuned off” or “tuned on” as the solvent dependent donor emission energy becomes in resonance with a charge transfer state or with the <sup>5</sup>L<sub>6</sub> Eu<sup>3+</sup> ion state resulting in

non-radiative decay or with  $^5L_6$  state of the  $\text{Eu}^{3+}$  ion resulting in radiative decay. For example, energy transfer from  $\text{Cu}(\text{CN})_2^-$  donor clusters to  $\text{Tb}^{3+}$  acceptor ions was observed in methanolic solutions, whereas no energy transfer was observed in acetonitrile solutions.

4. Lu, H.\*; Yson, R.\*; Ford, J.†; Tracy, H. J. †; Carrier, A. B.†; Keller, A.†; Mullin, J. L.‡; Poissan, M. J.‡; Sawan, S.‡; Patterson, H. H.\* Tunable energy transfer from  $d^{10}$  heterobimetallic dicyanide(I) donor ions to terbium(III) acceptor ions in luminescent  $\text{Tb}[\text{Ag}_x\text{Au}_{1-x}(\text{CN})_2]_3$  ( $x = 0 \rightarrow 1$ ). *Chem. Phys. Lett.* **2007**, 443, 55.

\*Department of Chemistry, University of Maine, Orono, Maine 04469; †Department of Chemistry, University of Southern Maine, Portland, Maine 04104; ‡Department of Chemistry & Physics, University of New England, Biddeford, Maine 04005.

**Summary:** In this paper, we reported on the heterobimetallic system,  $\text{Tb}[\text{Ag}_x\text{Au}_{1-x}(\text{CN})_2]_3$  ( $x = 0 \rightarrow 1$ ) in which sensitization of terbium luminescence occurs by energy transfer from  $[\text{Ag}_x\text{Au}_{1-x}(\text{CN})_2]^-$  donor excited states. The donor states have energies which are tunable and dependent on the Ag/Au stoichiometric ratio. We report on their use as donor systems with Tb(III) ions as acceptor ions in energy transfer studies. Luminescence results show that the mixed metal dicyanides with the higher silver loading have a better energy transfer efficiency than the pure  $\text{Ag}(\text{CN})_2^-$  and  $\text{Au}(\text{CN})_2^-$  donors. The better energy transfer efficiency is due to the greater overlap between the donor emission and acceptor excitation.

5. Hettiarachchi, S. R.\*; Schaefer, B. K.\*; Yson, R. L.; Staples, R. J.†; Herbst-Irmer, R.‡; Patterson, H. H.\* Observation of a mixed metal transition in heterobimetallic Au/Ag dicyanide systems. *Inorg. Chem.* **2007**, 46, 6997

\*Department of Chemistry, University of Maine, Orono, Maine 04469; †Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St., Cambridge, MA 02138, USA; ‡Department of Structural Chemistry, University of Göttingen, Tammannstr. 4,

D-37077 Göttingen, Germany.

**Summary:** Crystals of the mixed metal heterobimetallic Au/Ag dicyanide complex,  $K[Au_xAg_{1-x}(CN)_2]$  ( $x = 0 \rightarrow 1$ ), crystallizes in a rhombohedral crystal system, space group  $R\bar{3}$ . The crystal structure consists of layers of linear chains of  $Au(CN)_2^-$  and  $Ag(CN)_2^-$  ions, and  $K^+$  ions that connect the layers through the N atoms. The excitation and emission spectra of single crystals of  $K[Au_xAg_{1-x}(CN)_2]$  were recorded at 4.2 - 180 K using excitation wavelengths between 230 and 260 nm. Two emission bands due to Ag-Au interactions were observed at 343 and 372 nm. Lifetime measurements indicate the shorter wavelength emission corresponds to fluorescence and the longer

wavelength band is phosphorescence. These new emission bands are not seen in the pure  $K[Ag(CN)_2]$  or pure  $K[Au(CN)_2]$  crystals. Molecular orbital calculations show that the LUMO of the mixed metal system is bonding while the HOMO is antibonding or very weakly bonding. Moreover, excited state calculations indicate the formation of exciplexes with shorter metal-metal distances and higher metal-metal overlap populations than the corresponding ground state oligomers. The luminescence is assigned to a mixed metal transition from a molecular orbital with Au character to a molecular orbital with Ag character.

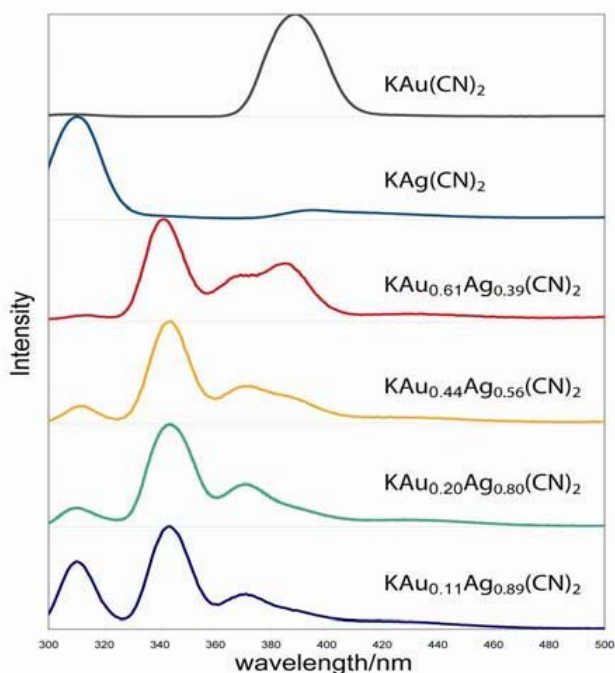


Figure 3 Emission Spectra of  $K[Au_xAg_{1-x}(CN)_2]$  ( $x = 0 \rightarrow 1$ ) at 4.2 K with  $\lambda_{ex} = 265$  nm as the metal composition is changed. Emission bands at 343 and 372 nm appear in the mixed metal systems and not in the pure metal systems and are assigned to mixed metal transitions.

- Arvapally, R. K.\*; Sinha, P.\*; Hettiarachchi, S.R.†; Coker, N.L.‡; Bedel, C.E.‡; Patterson, H. H.†; Elder, R.C.‡; Wilson, A.K.\*; Omary, M.A.\* Photophysics of bis(thiocyanato)gold(I) complexes: Intriguing structure luminescence relationships. *J. Phys. Chem. C*. **2007**, 111, 10689

\*Department of Chemistry, University of North Texas, Denton, Texas, 76203; †Department of Chemistry, University of Maine, Orono, Maine 04469; ‡Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172.

**Summary:** The electronic structure of bis(thiocyanato)gold(I) complexes is studied both experimentally and theoretically. Temperature dependent photoluminescence studies for  $K[Au(SCN)_2]$  reveal two unstructured luminescence bands: a strong green phosphorescence band ( $t_{77\text{K}} = 45.4\text{ ms}$ ) and a weak blue fluorescence band ( $t_{77\text{K}} = 24.4\text{ ns}$ ) that becomes well resolved by cooling toward 4 K or by time-resolved measurements, representing a rare case for Au(I) compounds whereby both fluorescence and phosphorescence are observed simultaneously. Quantum mechanical calculations for dimeric models indicate Au–Au covalent bond formation in the T1 lowest triplet excited state ( $2.62\text{ \AA}$ ;  $u_{\text{Au-Au}} = 180\text{ cm}^{-1}$ ), compared

to corresponding values of  $2.95\text{ \AA}$  and  $84\text{ cm}^{-1}$ , respectively, for the aurophilically bound  $S0$  ground state. Intriguing structure–luminescence relations exist for bis(thiocyanato)gold(I) complexes with different cations such as  $K^+$ ,  $Rb^+$ ,  $n\text{-Bu}_4\text{N}^+$ , and  $Cs^+$  in which the salts with shorter Au⋯Au nearest neighbor separations show blue shifts in the phosphorescence emission energies as well as smaller Stokes' shifts, contrary to the expected trends. We have also observed significantly red-shifted phosphorescence energies and larger Stokes shifts in frozen solutions of  $K[Au(SCN)_2]$  compared to those for the crystals. The computational data suggest that the emission energy is sensitive to the counterion, in support of the experimental photoluminescence data. Full optimizations of the T1 states for isolated dimeric models in vacuum predict a drastic rearrangement in the T1 states in contrast to the  $S0$  ground state and provide a physical basis for understanding the experimental photophysical results for this class of compounds.

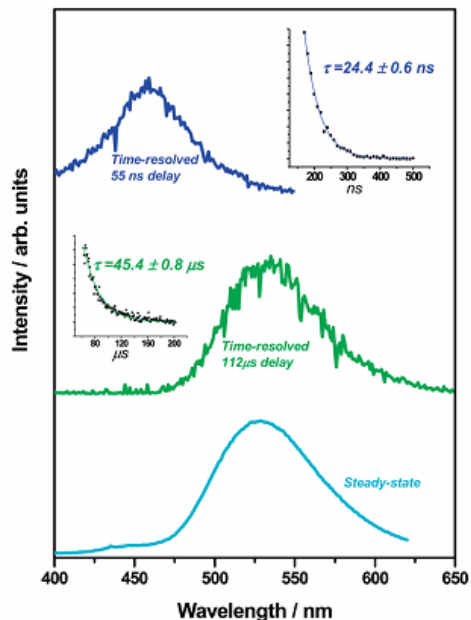


Figure 4 Time-resolved spectra showing the resolution of the fluorescence and phosphorescence bands for crystalline  $K[Au(SCN)_2]$ .

7. Katz, M.J.\*; Michaelis, V.K.†; Aguiar, P.M.†; Yson, R.‡; Lu, H.‡; Kaluarachchi, H.\*; Batchelor, R.J.\*; Kroeker, S.†; Patterson, H. ‡; Leznoff, D.B.\* Structural and spectroscopic impact of tuning the stereochemical activity of the lone pair in lead(II) cyanoaurate coordination polymers via ancillary ligands. *Inorg. Chem.* **2008**, *47*, 6353.

\*Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada V5A 1S6; †Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada R3T 2N2; ‡Department of Chemistry, University of Maine, Orono, ME 04469.

**Summary:** The synthesis of coordination polymers has been of great interest in recent years due to their interesting topological structures and their associated physical properties. The modular synthesis of these polymers offers the ability to choose building blocks that can incorporate a wide range of metals and bridging ligands in the process leading to design of specific structures with pre-defined properties. In making such choices, factors taken into consideration include the geometric preference of the metals used, the geometry and denticity of both the bridging and ancillary ligand (if any) on the metal. In general most ancillary ligands are innocent, playing the key role of controlling the dimensionality and topology of the final polymer by limiting the number of open coordination sites and their orientation. With  $d^{10}s^2$  metals such as lead(II), which feature in a range of materials with non-linear optical (NLO), ferroelectric, and semiconductor properties, an additional element of structural control can be tuned: the stereochemical activity of the lone-pair. If stereochemically active, the lone-pair occupies and blocks a portion of the lead(II) coordination sphere, thereby effectively altering the orientation of the remaining coordination sites for bridging ligands to occupy; if inactive, a more symmetric geometry becomes available. An in-depth study of lead(II) coordination compounds attributed the presence or absence of a stereochemically active lone-pair to several factors, including the Lewis-base character of the ancillary ligand, and the degree of ligand to metal charge transfer. More basic constituents around the lead(II) center induce more mixing of the 6p orbital with the 6s-orbital, leading to a stereochemical lone pair. Thus, lead(II) structures can be categorized as hemi- or holo-directional. From X-ray crystallographic data, hemi-directional structures have physical evidence that the lone-pair is stereochemically active, usually in the form of unusual bond lengths around the coordination sphere of the lead(II). Holo-directional lead(II) complexes show much more symmetrical coordination spheres and bond lengths. The key point is that a judicious choice of

ancillary ligand in conjunction with lead(II) may fine-tune the 6p-character in the 6sp-hybrid orbital, thereby impacting the structure and properties of the resulting coordination polymer.

8. Lu H.<sup>†‡</sup>; Yson R.<sup>‡ §</sup>; Li X.<sup>‡</sup>; Larochelle, C.<sup>|</sup>; Patterson H. H.<sup>\*‡</sup> Luminescent Studies of “Exciplex Tuning” for Nanoclusters of Dicyanocuprate(I) Ions Doped in Potassium Chloride Crystals *J. Phys. Chem. C. In press*

College of Chemistry, Jilin University, Changchun, 130012, P. R. China, Department of Chemistry, University of Maine, Orono, Maine 04469, Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557 and Department of Physics, Franklin & Marshall College, Lancaster, Pennsylvania 17604

**Summary:** The photoluminescence behavior of nanoclusters of dicyanocuprate(I) ions doped in KCl host crystals has been studied. Several ultraviolet and visible emission bands are observed in this system. Each emission band becomes dominant at a characteristic excitation wavelength; that is, the energy of the emission can be tuned by site-selective spectroscopy. The experimental evidence includes the broadness, the absence of detailed structure and the very low band energies of the luminescence bands. The emission bands are assigned to different  $^*[\text{Cu}(\text{CN})_2^-]_n$  luminescent nanocluster exciplexes. Tuning of the emission over the 220-500 nm range has been achieved by site-selective excitation in a single KCl:Cu(CN)<sub>2</sub><sup>-</sup> crystal. *Ab initio* molecular orbital calculations have been carried out to aid in assigning the different observed luminescence bands to different nanoclusters. We have used computer modeling to predict the relative stabilities of Cu nanoclusters in different alkali halide.