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# Photophysical and Photochemical Investigations of New Tunable Luminescent Metal-Metal Bonded d8-d10 Exciplexes

Howard H. Patterson

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**Final Report for Period:** 08/2010 - 07/2011**Submitted on:** 09/20/2011**Principal Investigator:** Patterson, Howard H.**Award ID:** 0715266**Organization:** University of Maine**Submitted By:****Title:**

Photophysical and Photochemical Investigations of New Tunable Luminescent Metal-Metal Bonded d8-d10 Exciplexes

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

Howard Patterson supervised the team of undergraduate students, graduate students and post-doctoral research associates actively working toward the development of new nanosystems.

**Post-doc****Name:** Baril-Robert, Francois**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Francois Baril-Robert is a postdoc working on the synthesis, spectroscopic characterization and theoretical calculation of new mixed-metal nanosystems.

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

Xiaobo Li is a graduate student working on this NSF project and doing studies of d8-d10 nanosystems. He is supported by NSF funds.

**Name:** Welch, David**Worked for more than 160 Hours:** Yes**Contribution to Project:**

David Welch is modeling formation of nanoclusters of d10 ions in alkali halide hosts.

**Undergraduate Student****Name:** Nicholas, Aaron**Worked for more than 160 Hours:** Yes**Contribution to Project:**Aaron Nicholas has studied energy transfer from d8 and d10 donor ions to Eu<sup>3+</sup>, Tb<sup>3+</sup> and other lanthanide acceptor ions in bulk mixed-metal compounds.**Name:** Record, Michael**Worked for more than 160 Hours:** No**Contribution to Project:**

Micheal Record has worked on the synthesis of mixed-metal bulk systems containing lanthanide ions as energy acceptor.

**Name:** Wong, Linda**Worked for more than 160 Hours:** No**Contribution to Project:**

Linda Wong worked on the synthesis of mixed-metal nanosystems.

**Name:** Cookson, Nathan

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

**Contribution to Project:**

Nathan Cookson has studied the luminescence enhancement processes (energy transfer, excited state coupling) in mixed metal solutions.

**Name:** Furman, Matthew

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

**Contribution to Project:**

Matthew Furman worked on the luminescence characterization of d8+d10 mixed metal nanosystems.

**Technician, Programmer**

**Other Participant**

**Research Experience for Undergraduates**

**Organizational Partners**

**University of North Texas**

Collaborative research has been carried out with Professor Mohammad Omary, who was a former student in my group. We are continuing temperature dependent studies of optical memory for both  $K_2Na[Ag(CN)_2]$  and  $M[Au(SCN)_2]$  ( $M = K$  or  $Na$ ) with Professor Omary and his students.

**Simon Fraser University**

Collaborative research has been carried out with Professor Leznoff. and one paper has been submitted with the title 'Changes in electronic properties of polymeric 1D  $\{[M(CN)_2]_n$  ( $M = Au, Ag$ ) chains due to neighboring closed-shell Zn(II) or open-shell Cu(II) ions' by Fran?ois Baril-Robert, Xiaobo Li, Michael J. Katz, Andrew R. Geisheimer, Daniel B. Leznoff, Howard Patterson to Inorg. Chem.

**Franklin and Marshall College**

Collaborative research has been carried out with Professor Larochelle, who was a former student in my group. One paper has been published with the title 'Luminescent Studies of 'Exciplex Tuning' for Nanoclusters of Dicyanocuprate(I) Ions Doped in Potassium Chloride Crystals' by Haiyan Lu, Renante Yson, Xiaobo Li, Christie Larochelle, and Howard H. Patterson in J. Phys. Chem. C, 2009, 113, 5952. and one paper has been accepted with the title 'Site-Selective Excitation of 'Exciplex Tuning' for Luminescent Nanoclusters of Dicyanoargentate (I) Ions Doped in Different Alkali Halide Crystals' by Baril-Robert, F.; Li, X.; Welch, D. A.; Schneider, B. Q.; O'Leary, M.; Larochelle, C. L.; Patterson, H. H. in J. Phys. Chem. C.

**College of William and Mary**

Collaborative research has been carried out with Professor Pike and his students of the Department of Chemistry, College of William and Mary. The research is focused on the structural and electronic properties of copper cyanide exposed to amines or imines (gas and liquids). Two papers have been published with the title 'Reversible Luminescent Reaction of Amines with Copper(I) Cyanide' by Ley, A. N.; Dunaway, L. E.; Brewster, T. P.; Dembo, M. D.; Harris, T. D.; Baril-Robert, F.; Li, X.; Patterson, H. H.; Pike, R. D. in Chem. Comm. 2010, 46, 4565 and 'Structure and Luminescence of Copper(I) Cyanide?Amine and ?Sulfide Networks' by Dembo, M. D.; Dunway, L. E.; Jones, J. S.; Lepekhina, E. A.; McCullough, S. M.; Ming, J. L.; Li, X.; Baril-Robert, F.; Patterson, H. H.; Bayse, C. A.; Pike, R. D in Inorg. Chim. Acta (online)

**University of Karlsruhe**

Collaborative research has been carried out with Professor Annie K. Powell. We are studying the photo-induced electron transfer process between gold dicyanide and an organic chromophore of the diviologen family. One paper has been submitted with the title 'Synthesis, Structure and optical properties of  $[Au(CN)_2]$ - Dimeric networks trapped in an Electron-acceptor Organic Framework' by Abouelwafa, A. S.; Anson, C. E.; Hauser, A.; Patterson, H. H.; Baril-Robert, F.; Powell, A. K. to J. Am. Chem. Soc..

**The American University of Sharjah**

Collaborative research has been carried out with Professor Sofian Kanan, who was a former student in my group. One paper is to be submitted with the title 'A Study of the Effect of Microwave Treatment on Metal Zeolites and Their Use as Photocatalysts Toward Naptalam' by Kanan, S. M.; Abdo, N.; Khalil, M.; Li, X.; Abu-Yousef, I. A.; Baril-Robert, F.; Patterson, H. H. to J. Phys. Chem. C.

### Other Collaborators or Contacts

### Activities and Findings

#### **Research and Education Activities:**

In the past year, our research group has completed projects and undertaken new experiments in relation with the research field described in the proposal (CHE-0715266). This report summarizes new results that led to published papers, conference presentation, manuscripts in the making and research collaboration. The attached file enumerates different projects that were done this year.

#### **Findings: (See PDF version submitted by PI at the end of the report)**

See attached file.

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

#### **Outreach Activities:**

### Journal Publications

Lu, HY; Yson, R; Li, XB; Larochelle, C; Patterson, HH, "Luminescent Studies of "Exciplex Tuning" for Nanoclusters of Dicyanocuprate(I) Ions Doped in Potassium Chloride Crystals", JOURNAL OF PHYSICAL CHEMISTRY C, p. 5952, vol. 113, (2009). Published, 10.1021/jp808910

Baril-Robert, F; Guo, ZH; Patterson, HH, "Study of the energy transfer process in the highly luminescent heterometallic dimers of Ce<sup>3+</sup> and d(10) [Ag(CN)<sub>2</sub>]<sup>-</sup> or d(8) [Pt(CN)<sub>4</sub>]<sup>(2-)</sup> ions", CHEMICAL PHYSICS LETTERS, p. 258, vol. 471, (2009). Published, 10.1016/j.cplett.2009.02.03

Baril-Robert, F; Palla, V; Li, XB; Yson, R; Patterson, HH, "Observation of a mixed-metal transition in a d(8)-d(10) heterobimetallic Pt-Ag cyanide system: Experimental and theoretical study", INORGANICA CHIMICA ACTA, p. 2637, vol. 363, (2010). Published, 10.1016/j.ica.2010.05.00

Ley, AN; Dunaway, LE; Brewster, TP; Dembo, MD; Harris, TD; Baril-Robert, F; Li, XB; Patterson, HH; Pike, RD, "Reversible luminescent reaction of amines with copper(I) cyanide", CHEMICAL COMMUNICATIONS, p. 4565, vol. 46, (2010). Published, 10.1039/c002351

Dembo, MD; Dunaway, LE; Jones, JS; Lepekhina, EA; McCullough, SM; Ming, JL; Li, XB; Baril-Robert, F; Patterson, HH; Bayse, CA; Pike, RD, "Structure and luminescence of copper(I) cyanide-amine and -sulfide networks", INORGANICA CHIMICA ACTA, p. 102, vol. 364, (2010). Published, 10.1016/j.ica.2010.07.07

Baril-Robert, F; Li, XH; Weleh, DA; Schneider, BQ; O'Leary, M; Larochelle, CL; Patterson, HH, "Site-Selective Excitation of "Exciplex Tuning" for Luminescent Nanoclusters of Dicyanoargentate(I) Ions Doped in Different Alkali Halide Crystals", JOURNAL OF PHYSICAL CHEMISTRY C, p. 17401, vol. 114, (2010). Published, 10.1021/jp105155

Welch, D. A.; Baril-Robert, F.; Li, X.; Patterson, H. H., "Luminescence and simulation of mixed metal nanoclusters of dicyanoargentate(I) and dicyanoaurate(I) in alkali halides", Inorg. Chim. Acta, p. 279, vol. 370, (2011). Published,

Baril-Robert, F.; Li, X.; Katz, M. J.; Geisheimer, A. R.; Leznoff, D. B.; Patterson, H. H., "Changes in electronic properties of polymeric 1D {[M(CN)<sub>2</sub>]-}<sub>n</sub> (M = Au, Ag) chains due to neighboring closed-shell Zn(II) or open-shell Cu(II) ions", *Inorg. Chem.*, p. 231, vol. 50, (2011). Published,

Kanan, S. M.; Abdo N.; Khalil, M.; Li, X.; Abu-Yousef, I. A.; Baril-Robert, F.; H. H. Patterson, "A study of the effect of microwave treatment on metal zeolites and their use as photocatalysts toward naptalam", *Appl. Catal. B.*, p. 350, vol. 106, (2011). Published,

Miller, K. M.; McCullough, S. M.; Lepekhina, E. A.; Thibau, I. J.; Pike R. D.; Li, X.; Killarney, J. P.; Patterson, H. H., "Copper(I) Thiocyanate-amine networks: synthesis, structure, and luminescence behavior", *Inorg. Chem.*, p. 7239, vol. 50, (2011). Published,

Gomez, R. S.; Li, X.; Yson, R. L.; Patterson, H. H., "Zeolite-supported silver and silver-iron nanoclusters and their activities as Photodecomposition Catalysts", *Res. Chem. Intermediat.*, p. , vol. , (2011). Accepted,

Abouelwafa, A. S.; Anson, C. E.; Hauser, A.; Patterson, H. H.; Baril-Robert, F.; Li, X.; Powell, A. K., "Photophysical properties of {[Au(CN)<sub>2</sub>]-}<sub>2</sub> dimers trapped in a supramolecular electron-acceptor organic framework", *Inorg. Chem.*, p. , vol. , (2011). Submitted,

### Books or Other One-time Publications

#### Web/Internet Site

#### Other Specific Products

#### Contributions

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

- ' Luminescent detection of amines and imines using copper(I) cyanide. ' 238th ACS National Meeting, Washington, DC, United States, Aug. 2009, Pike, Robert D.; Ley, Amanda N.; Jones, James S.; Dunaway, Lars E.; Dembo, Matthew D.; Bayse, Craig A.; Baril-Robert, Francois; Patterson, Howard H.
- ' Luminescence studies of 'exciplex tuning' for nanoclusters of dicyanoargentate(I) ions doped in different alkali halides' 238th ACS National Meeting, Washington, DC, United States, Aug. 2009, Patterson, Howard H.; Baril-Robert, Francois; Larochelle, Christie L.; Li, Xiaobo; Welch, David.
- ' Photophysical and photochemical investigations of new tunable luminescent metal-metal bonded d8-d10 exciplex nanoclusters doped in alkali halides' 238th ACS National Meeting, Washington, DC, United States, Aug. 2009, Baril-Robert, Francois; Li, Xiaobo; Larochelle, Christie L.; Welch, David; Patterson, Howard H.
- ' Luminescent nitrogen and sulfur adducts of copper(I) salts' 240th ACS National Meeting, Boston, MA, United States, Aug., 2010, Pike, Robert D.; McCullough, Shannon M.; Safko, Jason P.; Dunaway, Lars E.; Dembo, Matthew D.; Patterson, Howard H.; Bayse, Craig A.
- ' Spectroscopic study of heterometallic d8-d10 and d10-d10 exciplex nanoclusters doped in alkali halide single crystals' 240th ACS National Meeting, Boston, MA, United States, Aug., 2010, Patterson, Howard H.; Baril-Robert, Francois; Li, Xiaobo; Welch, David A.; Larochelle, Christie L.
- ' Nanoclusters of dicyanocuprate (I) ions doped in different alkali halides' 240th ACS National Meeting, Boston, MA, United States, Aug., 2010, Li, Xiaobo; Welch, David A.; Baril-Robert, Francois; Patterson, Howard H.
- ' Structural host effects on the nature of mixed-metal interactions in nanoclusters of dicyanoargentate(I) and dicyanoaurate(I) ions doped in different alkali halides' 240th ACS National Meeting, Boston, MA, United States, Aug., 2010, Patterson, Howard H.; Welch, David A.; Baril-Robert, Francois; Li, Xiaobo

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

Nothing (Yet) to Report

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

One female and six males have been trained in our laboratory on common spectroscopy instrumentation for electronic and physical structure investigations.

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

Nothing (Yet) to Report

**Contributions Beyond Science and Engineering:**

Nothing (Yet) to Report

**Conference Proceedings**

**Categories for which nothing is reported:**

Activities and Findings: Any Training and Development

Activities and Findings: Any Outreach Activities

Any Book

Any Web/Internet Site

Any Product

Any Conference

1. Baril-Robert, F.; Palla, V.; Li, X.; Yson, R.; Patterson, H. H. "Observation of a Mixed-Metal Transition in a  $d^8$ - $d^{10}$  Heterobimetallic Pt-Ag Cyanide System: Experimental and Theoretical Study", *Inorg. Chim. Acta* **2010**, 363, 2637

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

Photoluminescence spectra of synthesized crystals of the mixed-metal heterobimetallic  $Ba\{[Ag(CN)_2]_{2-2x}[Pt(CN)_4]_x\}$  ( $x = 0 \rightarrow 1$ ) were recorded at 300, 150 and 77 K. Emission of the mixed-metal system containing both  $[Pt(CN)_4]^{2-}$  and  $[Ag(CN)_2]^-$  ions shows an emission band due to Pt-Ag interaction. This new peak (424 nm) is not seen for pure  $Ba[Pt(CN)_4]$  or  $Ba[Ag(CN)_2]_2$ . Theoretical DFT and EHMO population calculations show that in heterometallic dimers, the HOMO correspond to  $d_{z^2}$  of the metals with a weakly antibonding interaction between the moieties while the LUMO  $\pi^*(CN)$  orbital shows a stronger bonding character between monomers. This indicates that the 424 nm emission peak corresponds to a MLCT ( $d \rightarrow \pi^*$ ) transition with some metal to metal charge transfer character (Pt to Ag). Fig 1 shows the energy diagram of the mixed-metal transition with MLCT/MMCT character for the  $Ba\{[Ag(CN)_2]_{2-2x}[Pt(CN)_4]_x\}$  ( $x = 0 \rightarrow 1$ ) system.

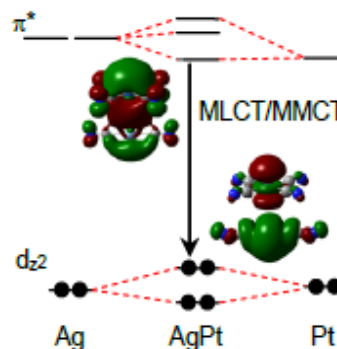


Fig. 1 Mixed-metal transition in  $Ba\{[Ag(CN)_2]_{2-2x}[Pt(CN)_4]_x\}$  ( $x = 0 \rightarrow 1$ )

2. Ley, A. N.<sup>\*</sup>; Dunaway, L. E.<sup>\*</sup>; Brewster, T. P.<sup>\*</sup>; Dembo, M. D.<sup>\*</sup>; Harris, T. D.<sup>†</sup>; Baril-Robert, F.<sup>‡</sup>; Li, X.<sup>‡</sup>; Patterson, H. H.<sup>‡</sup>; Pike, R. D.<sup>\*</sup> “Reversible Luminescent Reaction of Amines with Copper(I) Cyanide”, *Chem. Comm.* **2010**, 46, 4565

<sup>\*</sup>: Department of Chemistry, College of William and Mary, Williamsburg, VA 23187

<sup>†</sup>: Department of Chemistry, University of California, Berkeley, CA 94720

<sup>‡</sup>: Department of Chemistry, University of Maine, Orono, ME 04469

Copper(I) cyanide exposed to various liquid or vapor-phase amines (L) at ambient temperature produces a variety of visible photoluminescence colors via reversible

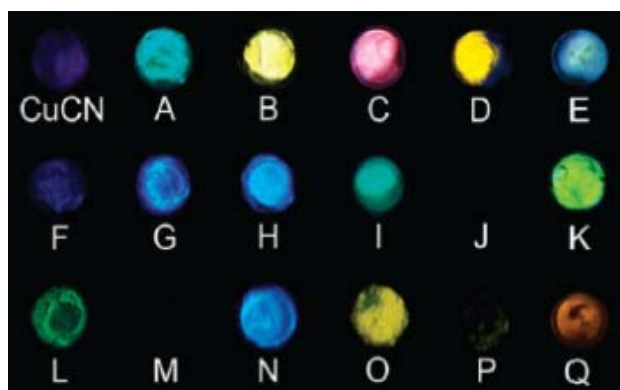


Fig. 2 Luminescence of CuCN + liquid L under 254 nm light at room temperature. A: Pipd, B: N-MePipd, C: N-Et-Pipd, D: NMePyrrolidine, E: Me2NCy, F: NEt3, G: N-MeMorph, H: N-MePipz, I: N,N0-e2Pipz, J: Py, K: 2-MePy, L: 3-MePy, M: 4-MePy, N: 2-EtPy, O: 3-EtPy, P: 4-EtPy, Q: 4-tBuPy.

= pyridine) While CuCN produces barely visible luminescence emission centered at 392 nm, the CuCN samples exposed to many liquid or vapor amines show luminescence at wavelengths shifted well into the visible region. The CuCN luminescence wavelength modulated by various incoming ligands suggests that this system might provide the foundation for an amine vaporsensing device.

formation of amine adducts. The adducts show phase matches to authentic (CuCN)<sub>n</sub>, n = 0.75-2.0, produced by heating CuCN with liquid amine. Fig 2 shows the direct addition of amine (L) liquid or diffusion of amine vapor to solid CuCN at room temperature produces a variety of visible colored luminescence responses. (Pipd = piperidine, Cy = cyclohexyl, Morph = morpholine, Pipz = piperazine, Py



3. Dembo, M. D.<sup>\*</sup>; Dunway, L. E.<sup>\*</sup>; Jones, J. S.<sup>\*</sup>; Lepekhina, E. A.<sup>\*</sup>; McCullough, S. M.<sup>\*</sup>; Ming, J. L.<sup>†</sup>; Li, X.<sup>‡</sup>; Baril-Robert, F.<sup>‡</sup>; Patterson, H. H.<sup>‡</sup>; Bayse, C. A.<sup>†</sup>; Pike, R. D.<sup>\*</sup>  
 “Structure and Luminescence of Copper(I) Cyanide–Amine and –Sulfide Networks”,  
*Inorg. Chim. Acta* **2010**, *364*, 102

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<sup>†</sup>: Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529

<sup>‡</sup>: Department of Chemistry, University of Maine, Orono, ME 04469

Copper(I) cyanide reacts with various liquid amines and sulfides (L) under solvent-less conditions to form  $(\text{CuCN})_{L_n}$ ,  $n = 0.5, 0.57, 0.75, 0.8, 1, 1.25, 1.5, 2$ . New X-ray

structures are reported for L = Py (Py = pyridine,  $n = 0.57$ ), 2-MePy ( $n = 1$ ), 3-EtPy ( $n = 1.5$ ), 2-ClPy ( $n = 1$ ), 3-ClPy ( $n = 2$ ), 3-MeOPy ( $n = 2$ ), 4-tBuPy ( $n = 1.5$ ), piperidine ( $n = 1.25$ ), N-methylmorpholine ( $n = 1$ ), N,N-dimethylcyclohexylamine ( $n = 1$ ), 1-methylimidazole ( $n = 3$ ), Me<sub>2</sub>S ( $n = 1$ ), and tetrahydrothiophene ( $n = 1$ ). The amine structures (except for the

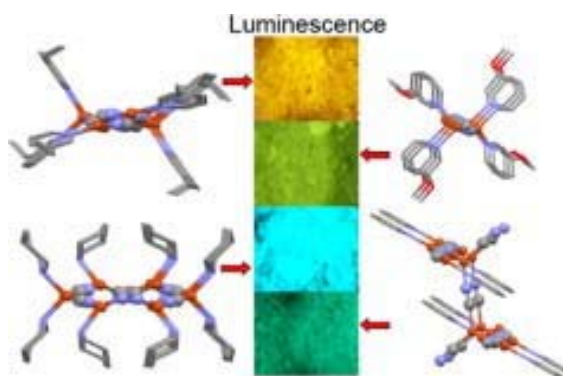


Fig 3 Luminescence of copper(I) cyanide reacts with amines and sulfides (L) to form ligand-decorated polymeric chains,  $(\text{CuCN})_{L_n}$  ( $n = 0.5-2$ ).

monomeric 1-methylimidazole complex) reveal 1D CuCN chains decorated with 0–2 L per metal atom. Chain structures observed include zigzag, helical and figure-8 helical. The CuCN-sulfide structures show sulfur-bridging of CuCN chains. In some cases  $(\text{CuCN})_{L_{\text{greater-or-equal, slanted}1.5}}$  species are transformed to  $(\text{CuCN})_L$  under vacuum. Thermal analysis shows facile release of ligand, yielding CuCN. Most of the  $(\text{CuCN})_{L_n}$  products are photoluminescent, emitting in the visible region, which is shown in Fig 3. In some cases, coordination of very similar amines results in remarkably different emission spectra.

4. Baril-Robert, F.\*; Li, X.\*; Welch, D. A.\*; Schneider, B. Q.\*; O’Leary, M.\*; Larochelle, C. L.†; Patterson, H. H.\* “Site-Selective Excitation of “Exciplex Tuning” for Luminescent Nanoclusters of Dicyanoargentate (I) Ions Doped in Different Alkali Halide Crystals”, *J. Phys. Chem.* **2010**, *114*, 17401

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†: Department of Physics and Astronomy, Franklin & Marshall College, Lancaster, PA 17604

Luminescent nanoclusters of linear dicyanoargentate(I) ions doped in different alkali halide single crystals (NaF, NaCl, NaBr and KCl) have been investigated. Site-selective excitation of the different nanoclusters results in the appearance of emission bands which are assigned to different luminescent  $\{[Ag(CN)_2]^{-}\}_n$  nanoclusters in the host lattices. The nanoclusters of  $[Ag(CN)_2]^{-}$  in the alkali halides display energy tunability over a wide wavelength interval. Fig 4 shows that with the variation of excitation wavelength, the

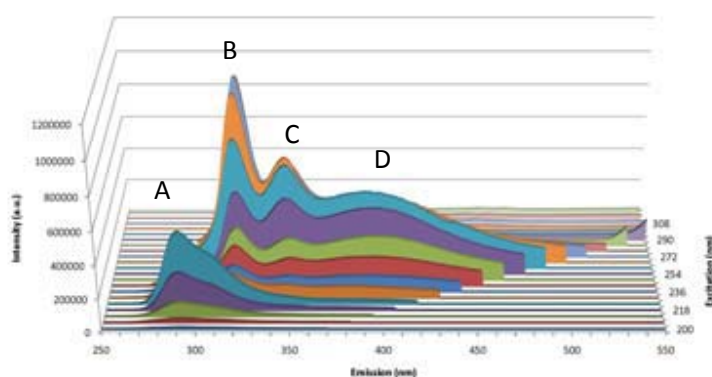


Fig4 Emission spectra ( $\lambda_{ex}$  = every 6nm) of a single crystal  $[Ag(CN)_2] \cdot NaCl$  (0.19 wt%) at 77K showing 4 different emission peaks [A( $\lambda_{ex}$  = 225nm,  $\lambda_{em}$  = 287nm); B( $\lambda_{ex}$  = 275nm,  $\lambda_{em}$  = 318nm); C( $\lambda_{ex}$  = 272nm,  $\lambda_{em}$  = 347nm); D( $\lambda_{ex}$  = 260nm,  $\lambda_{em}$  = 398nm)]

emission energy changes from 287 nm to 398 nm.

The ab initio DFT calculations show that for nanoclusters, the first excited state has a deeper potential and shorter internuclear separation than the nanocluster ground state, indicative of excimer/exciple behavior.

Molecular modeling

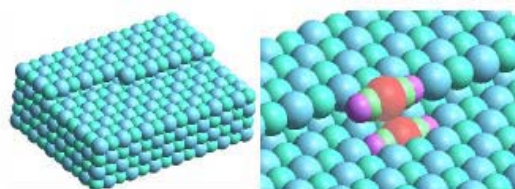
indicates how the distribution of nanoclusters varies with the host lattice. This emission energy tunability makes these systems attractive candidates for potential applications, such as tunable solid state lasers, photocatalysts and photosensitizers for water splitting.

5. Welch, D. A.; Baril-Robert, F.; Li, X.; Patterson, H. H. "Luminescence and Simulation of Mixed Metal Nanoclusters of Dicyanoargentate(I) and Dicyanoaurate(I) in Alkali Halides", *Inorg. Chim. Acta* **2011**, 370, 279

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

Heterometallic and homometallic nanoclusters of  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$  doped in NaCl, KCl, and NaBr exhibit interesting photophysical phenomenon that are related to the variety of sizes, orientations, and compositions these clusters adopt. Samples of various dopant-host systems have been grown and analyzed with luminescence spectroscopy. In order to predict what types of clusters are in these different systems, an atomistic surface model which is

shown in Fig 5, has been developed that probes the energetics of these clusters as they first form at surface kink sites. An order of preference in mixed-metal systems for heterometallic cluster formation over homometallic cluster formation,



*Fig 5 Representation of a 10 x 14 x 5 ideal alkali halide slab (left) and of a metal dicyanide dimer at its kink site (right). The metal atoms and cyanide ligands of the impurity complexes substitute for host cations and anions, respectively, at the kink site.*

NaBr > NaCl > KCl, is predicted which agrees with findings on heterometallic cluster peaks in the luminescence spectra. Structural orientations are predicted to be very different in heterometallic clusters as opposed to homometallic clusters.

6. Baril-Robert, F.<sup>\*</sup>; Li, X.<sup>\*</sup>; Katz, M. J.<sup>†</sup>; Geisheimer, A. R.<sup>†</sup>; Leznoff, D. B.<sup>†</sup>; Patterson, H. H.<sup>\*</sup> “Changes in Electronic Properties of Polymeric 1D {[M(CN)<sub>2</sub>]}<sub>n</sub> (M = Au, Ag) Chains due to Neighboring Closed-Shell Zn(II) or Open-shell Cu(II) Ions”, *Inorg. Chem.* **2011**, *50*, 231

<sup>\*</sup>: Department of Chemistry, University of Maine, Orono, ME 04469

<sup>†</sup>: Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A 1S6, Canada

A series of d<sup>10</sup> dicyanometallate polymeric compounds were studied by electronic spectroscopy and DFT calculations. Fig 6 shows the 2D structure of [Zn(en)<sub>2</sub>][Au(CN)<sub>2</sub>]<sub>2</sub>. The [Au(CN)<sub>2</sub>]<sup>-</sup> moieties form 1D chains via gold-gold interactions. The metallophilic 1D chains are crosslinked at every alternate [Au(CN)<sub>2</sub>]<sup>-</sup> unit by binding of both N-cyano donors to the axial positions of [Cu/Zn(en)<sub>2</sub>]<sup>2+</sup> cations to yield 1D chains of [(en)<sub>2</sub>Cu/Zn-NCAuCN]<sup>+</sup> units. In these materials, the negatively charged 1D polymeric chains are linked together by [M(en)<sub>2</sub>]<sup>2+</sup> (M = Cu(II) and Zn(II); en = ethylenediamine). More than innocent building blocks, the [M(en)<sub>2</sub>]<sup>2+</sup> units offer a possible synthetic way to modify electronic properties of the materials. Through its low energy d-d excited state, the d<sup>9</sup> copper(II) ions offers deactivation pathways for the normally emissive dicyanometallate polymer. Deactivation was shown to be specific to the excited state energy.

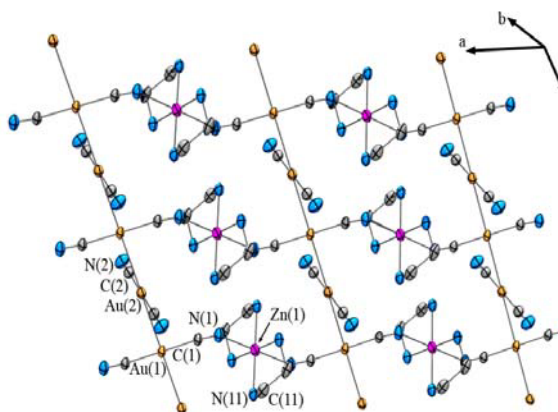


Fig 6 Representation of the 2D sheet structure of [Zn(en)<sub>2</sub>][Au(CN)<sub>2</sub>]<sub>2</sub>. Independent atoms are labeled.

7. Kanan, S. M.\*; Abdo, N.\*; Khalil, M.\*; Li, X.†; Abu-Yousef, I. A.\*; Baril-Robert, F.†; Patterson, H. H.† “A Study of the Effect of Microwave Treatment on Metal Zeolites and Their Use as Photocatalysts Toward Naptalam”, *Appl. Catal. B.* **2011**, *106*, 350

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A new route to fabricate silver and gold-based material incorporated into the Y zeolite framework is reported. X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), UV-Visible diffuse reflectance, and low-temperature steady-state photoluminescence spectroscopy indicate the formation of metallic silver and gold as well as  $\text{Ag}_n^{\text{m}+}$  clusters in the zeolite framework. Microwave treatment was found to affect the surface morphology and the metal content of the modified materials. The photodecomposition of the pesticide naptalam was enhanced in the presence of silver and

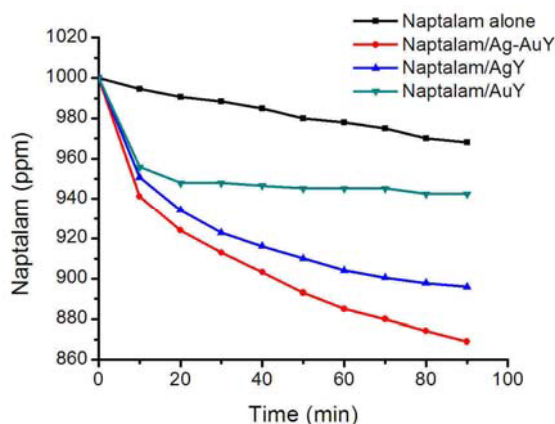


Fig 7 Hydrolysis profile obtained from HPLC analysis of 1.0 mL of 1000 ppm naptalam solution alone and in the presence of 5.0 mg of the indicated catalysts.

gold doped into zeolite Y catalysts. The largest catalytic activity was observed for the Ag-AuYm catalyst where the rate constant was found to be  $2.0 \times 10^{-3} \text{ s}^{-1}$  compared to the rate constant of  $1.0 \times 10^{-4} \text{ s}^{-1}$  calculated for the uncatalyzed irradiated naptalam solution. Fig 7 shows the changes that occur in the concentration of naptalam as a function of time depicted from the corresponding naptalams HPLC peak area. The microwave treated mixed sample (Ag-AuYm) acts as a good catalyst for the degradation of naptalam, however, the untreated sample (Ag-AuY) provides a selective surface that completely adsorbs naptalam from solution. GC-MS, HPLC, and SLS have indicated the formation of three products namely, naphthylamine, phthalic acid, and N-1-naphthylphthalimide for the photodecomposition of naptalam in aqueous solution. This is in contrast to the catalyzed reactions where N-1-naphthylphthalimide was the major product.

8. Miller, K. M.\*; McCullough, S. M.\*; Lepekhina, E. A.\*; Thibau, I. J.\*; Pike R. D.\*; Li, X.†; Killarney, J. P.†; Patterson, H. H.† “Copper(I) Thiocyanate-Amine Networks: Synthesis, Structure, and Luminescence Behavior”, *Inorg. Chem.* **2011**, *50*, 7239

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A series of metal-organic networks of CuSCN were prepared by direct reactions with substituted pyridine and

aliphatic amine ligands, L.

Thiocyanate bridging is

seen in all but one of

eleven new X-ray

structures. Structures are

reported for (CuSCN)L

sheets (L = 3-chloro- and 3-

bromopyridine, N-

methylmorpholine), ladders

(L = 2-ethylpyridine, N-

methylpiperidine), and

chains (L = 2,4,6-collidine).

X-ray structures of

(CuSCN)L<sub>2</sub> are chains (L = 4-ethyl- and 4-*t*-butylpyridine, piperidine, and morpholine).

A unique N-thiocyanato monomer structure, (CuSCN)(3-ethylpyridine)<sub>3</sub>, is also reported.

In most cases, amine ligands are thermally released at temperatures <100 °C. Strong

yellow-to-green luminescence at ambient temperature is observed for the substituted

pyridine complexes. Fig 8 shows luminescence spectra photographs under 365 nm light of pure CuSCN and with different amine ligands powder at 298 K. High solid state

quantum efficiencies are seen for many of the CuSCN-L complexes. Microsecond

phosphorescence lifetimes seen for CuSCN-L are in direct contrast to the nanosecond-

lifetime emission of CuSCN. MLCT associated with pyridine π\* orbitals is proposed as

the excitation mechanism.

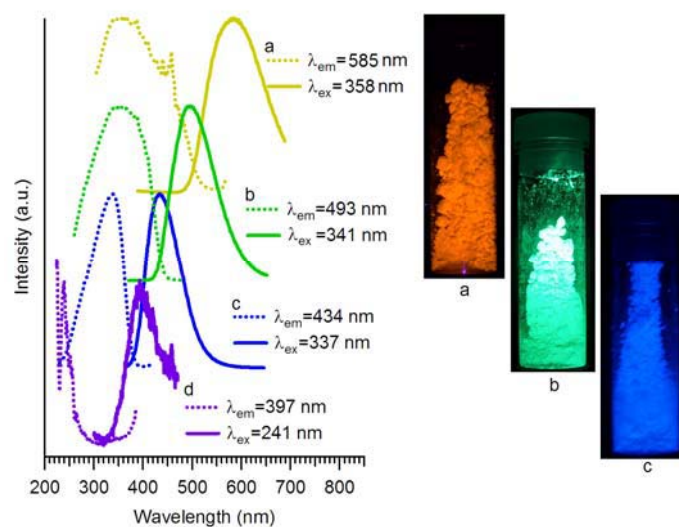


Fig 8 Luminescence spectra at 298 K and luminescence photographs under 365 nm light of (A) (CuSCN)(Quin)<sub>2</sub>, 7, (B) (CuSCN)(3MePy)<sub>2</sub>, 2, (C) (CuSCN)(26Lut), 8. (D) Luminescence spectra of pure CuSCN powder at 298 K.

9. Gomez, R. S.\*; Li, X.\*; Yson, R. L.†; Patterson, H. H.\* “Zeolite-supported silver and silver-iron nanoclusters and their activities as Photodecomposition Catalysts” *Res. Chem. Intermediate* **2011**, 37, 729

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Catalysts containing nanoclusters of Ag(I) and Fe<sub>2</sub>O<sub>3</sub> as dopants with sodalite and Y zeolite supports have been investigated in order to develop a more efficient catalyst for

photodecomposition of the pesticide carbaryl and to gain insight about the reaction mechanism. Ag(I)–sodalite, Ag(I)/Fe<sub>2</sub>O<sub>3</sub>–sodalite, Ag(I)–Y zeolite, and Ag(I)/Fe<sub>2</sub>O<sub>3</sub>–Y zeolite were synthesized by

ion-exchange techniques and characterized by powder X-ray diffraction (XRD), solid-

state luminescence, UV–visible absorption, and atomic absorption spectroscopy measurements. The luminescence activity of the sodalite-supported and Y zeolite-supported catalysts were significantly different, as shown in Fig 9. Catalyst performance studies were conducted using carbaryl as the target compound and specific wavelengths of UV light as photon sources for the experiments. The studies showed that each catalyst’s performance was determined primarily by the specific wavelength of the UV light with which the system was irradiated. The studies also showed that inclusion of Fe<sub>2</sub>O<sub>3</sub> as dopant enhanced the reactivity of the catalysts in several instances, with the Ag(I)/Fe<sub>2</sub>O<sub>3</sub>–sodalite catalyst and 298 nm irradiation being the most reactive of the systems studied. Additional reactions using each catalyst and 298 nm irradiation, and including either sodium bicarbonate as hydroxyl radical scavenger or D<sub>2</sub>O as solvent, showed that hydroxyl radicals were likely intermediates in the catalyzed photodecomposition reaction.

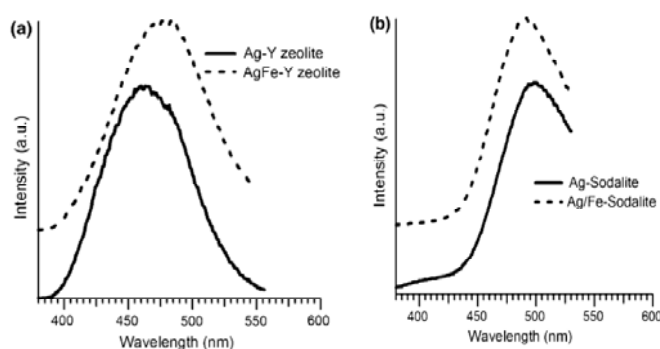


Fig 9 Solid-state luminescence emission spectra of Ag–Y and Ag/Fe–Y (a) and Ag–SOD and Ag/Fe–SOD (b) at 77 K and at 290 nm excitation. Addition of Fe(III) to the catalysts creates a slight red shift for Y-zeolite but a blue shift for sodalite



10. Abouelwafa, A. S.<sup>\*,†,‡</sup>; Anson, C. E.<sup>\*</sup>; Hauser, A.<sup>‡</sup>; Patterson, H. H.<sup>§</sup>; Baril-Rober, F.<sup>§</sup>; Powell, A. K.<sup>\*,†</sup> “Photophysical Properties of {[Au(CN)<sub>2</sub>]}<sub>2</sub> Dimers Trapped in a Supramolecule Electron-Acceptor Organic Framework”, *submitted to Inorg. Chem.*

<sup>\*</sup>: *Institut für Anorganische Chemie der Universität Karlsruhe, Karlsruhe Institute of Technology, Engesserstr. 15, D-76218 Karlsruhe, Germany*

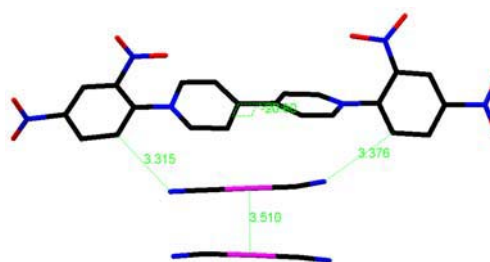
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<sup>‡</sup>: *Université de Genève, Département de Chimie Physique, 30 Quai Ernest Ansermet, CH-1211 Genève, Switzerland*

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Dicyanoaurate reacts with the organic acceptor, 1,1'-bis-(2,4-dinitrophenyl)-4,4'-bipyridinium, DNP to form a supramolecular complex with the general formula {[Au(CN)<sub>2</sub>]<sub>2</sub>DNP}·4H<sub>2</sub>O. The complex was characterized by X-ray crystallography and its photophysical properties were

investigated in the solid-state. Fig 10 shows a perspective view of the {(DNP)-[Au(CN)<sub>2</sub>]<sub>2</sub>} supramolecular complex. Although the starting (DNP)Cl<sub>2</sub> does not show any photoluminescence behavior and the dicyanoaurate shows fluorescence only in the UV range, the complex displays two simultaneous, almost independent



*Fig 10 A perspective view of the {(DNP)-[Au(CN)<sub>2</sub>]<sub>2</sub>} supramolecular complex showing the electrostatic interactions and short distances between the dicyanoaurate unit Au 1 and the dinitrophenyl peripheries of the {DNP} viologen from one side, and with the Au 2 unit from the other side*

photoluminescence in the visible range resulting from both the DNP unit and the dicyanoaurate dimers. The excitation spectra of the complex showed the presence of several bands in the UV range resulting from charge transfer behavior from the [Au(CN)<sub>2</sub>] donor units to the DNP acceptor. This unusual simultaneous photoluminescence displayed by both the dicyanoaurate donor units and the redox-active 4,4'-bipyridinium acceptor have life times of 0.5 μs and several hundred μs, respectively.