High Quantum Efficiency Coordination Polymers and Networks for OLED Application

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The objectives of this project are:

- understanding fundamental relationships between the components in self-organized electroluminescent coordination polymers,

- design of new electroluminescent materials, with enhanced efficiency and band width to span the visible spectrum

- and the synthesis of such materials for use in organic light-emitting diodes (OLEDs) for displays.

These materials are composed of emissive and electroluminescent complexes such as Alq3 with extended conjugated chromophores, and triplet acceptors, such as Pt(II)porphyrins. We showed it is possible to tune the emission of the Alq3-based metallocomplexes by changing the electronic nature of the substituents attached to the quinoline chromophore. A series of 5-aryl-quinolinolates Al(III) complexes with varying electronic nature was designed and successfully prepared (Fig.1).

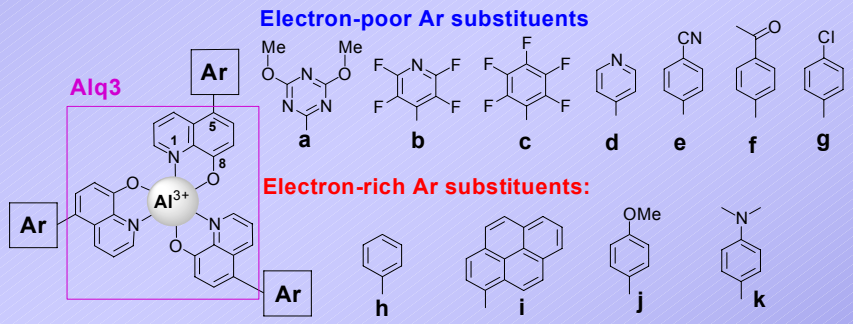
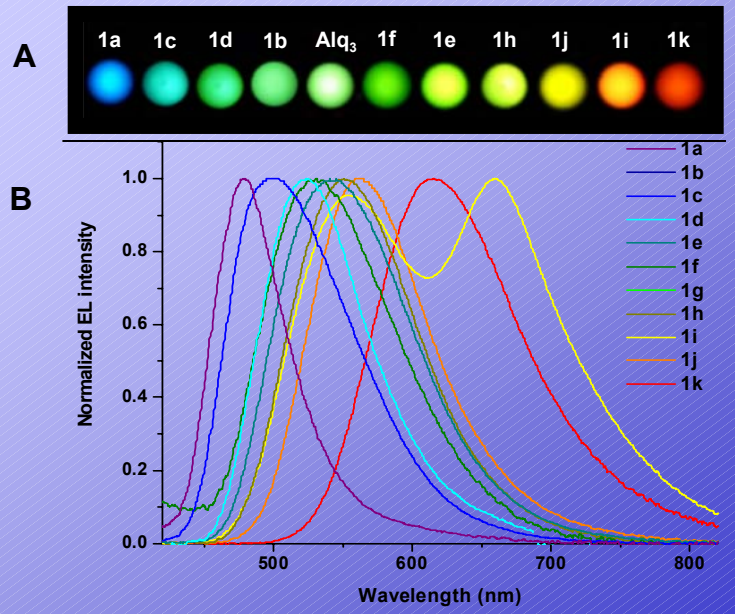


Fig.1. Effective blue-to-red emission tuning in solid state: Digital photograph (A) and electroluminescence spectra (B) from OLEDs fabricated using complexes 1a-k.



The goals of this project:

The objectives are the synthesis, understanding the fundamental relationships between components, structure, and topology in self-organized electroluminescent coordination polymers that can be potentially useful in the development of organic light-emitting diodes (OLEDs). The proposed multi-component materials are designed to process the energy of both singlet and triplet states of electroluminophores aimed at improving the efficacy of electroluminescence via transferring the energy of non-radiative triplet excited states to an emissive acceptor. Specifically, these materials will be composed of electroluminophores such as emissive bis(8-quinolinolate)(acetylacetonate)Al(III) (Alq2acac) complexes with extended conjugated chromophores, and triplet acceptors, such as Pt(II)porphyrins.

We proposed to synthesize two types of emissive coordination polymers. The first type of coordination polymers will be composed of two singlet state emitters such as Alq2acac, and oligomers of poly(1,4-phenylenevinylene) (PPV), polyarylene(PA), and poly(1,4-phenyleneethynylene) (PPE) types. Toward this end, we have synthesized various Aluminum quinolate complexes, studied their photophysical properties in solution, in solid state as well as in the actual OLEDs. The second type of coordination polymers will include Alq2acac complexes that will be connected to the triplet acceptors of matching energy through the conjugated oligomer. Such ternary coordination polymers consisting of two different singlet emitters/triplet donors (quinolinolate complex and a conjugated oligomer) and a triplet acceptor (Pt(II)porphyrin) will be used to study the energy transfer.

Studies of the first type of the coordination polymers are focused on understanding the optical and material properties of these singlet/singlet emitter materials, the second type of coordination polymers will be used to study the intercomponent energy transfer in the material. Specifically, the long-range singlet-singlet energy transfer between the Al-quinolinolate and Pt-porphyrin is expected to proceed via a Förster mechanism, while the singlet-triplet and triplet-triplet energy transfer proceed through a short-range Dexter mechanism. The role of the conjugated oligomer in the energy transfer mechanism, particularly the super-exchange versus the ‘bridge-mediated’ mechanism will be evaluated. The energy matching between the quinolinolate complex, the conjugated oligomer, and porphyrin will be used to optimize the Dexter-type energy transfer past the short range usually observed for this mechanism.

The results:

1. A series of 5-aryl-quinolinolates Al(III) complexes with varying electronic nature was designed and successfully prepared. The photophysical properties and electroluminescence of the novel materials were investigated. The preliminary study of the electroluminescent properties (EL) of OLEDs fabricated using the novel materials confirms our expectations that these complexes are, indeed, electroluminophores and, more importantly, that the EL spectra essentially reproduce the emission tuning pattern observed in solution. It was shown that the substituent electronic effects, when projected to the quinolinolate chromophore via an aromatic spacer, provide an effective tool for remarkable systematic emission color tuning of both the PL and EL over 300 nm (450-800 nm). Thus, the presence of an electron-withdrawing group (EWG) resulted in blue-shifted EL maxima while the presence of an electron-donating group (EDG) resulted in red-shifted EL. The fabricated devices displayed strong EL, suggesting that this approach could generate potentially useful OLED materials.

2. The performance of Aluminum metallocomplexes modified with acetylacetonate (*acac*) ligands was evaluated with respect to Alq3. The performance of diodes based on these materials was quite comparable to that of Alq3, with one of them displaying an external maximum efficiency, which clearly exceeds the performance of the parent material. We believe that these results represent an unambiguous proof that the charge transport properties of the complexes substituted with *acac* ligand are not being detrimentally affected at all.

3. To date we have synthesized two fluorene-hydroxyquinoline bridging ligands. Complexation of one of the bridging ligands with the aluminum source to generate the first coordination polymers was already attempted in two cases using ethanol and tetrahydrofuran as solvents. 1H NMR spectrum, Matrix-Assisted Laser Desorption Ionization – Time-Of-Flight analysis and Electron Spray Ionization-Mass Spectrometry suggest the formation of a discrete single molecule instead of a polymer. The spectral data from all used techniques seem to support the existence of a cyclic trimer instead of a linear oligomer. Photophysical studies of this material revealed relatively narrow emission ($\omega 1/2 \sim 110$nm) centered at about 560 nm with a quantum yield of 10.1%, and a mono-exponential lifetime of 8.00 ns.

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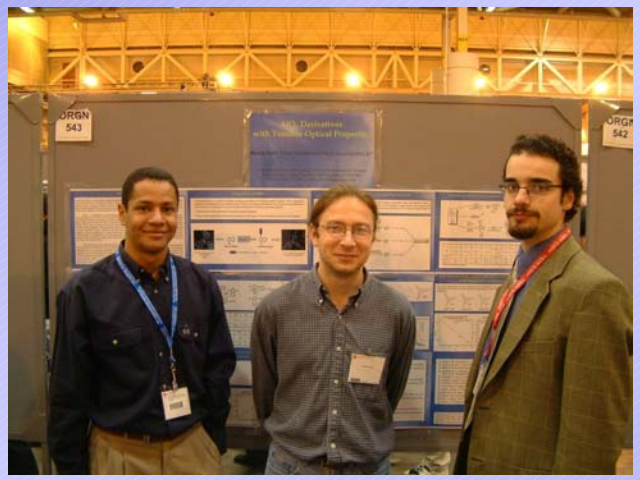
Education: The work on this project includes both graduate and undergraduate students as well as a post-doctoral associate who work together in this interdisciplinary field involving photochemistry, physics, and chemistry of materials. Also, we started a collaboration with Prof. J. Shinar's group of Iowa State University, who help us with fabrication of OLED devices from our compounds and provide their expertise to complement our group's knowledge.



Two of the PI's graduate students and a postdoc (middle) presenting results of their work at the ACS meeting.

Outreach: This PI is actively involved in summer programs focused on attracting minority students to study natural sciences.

Two undergraduate students have been involved in the work on this project. One student (Cesar Perez) who participated in the REU program spent the summer of 2003 in our research group. During the summer of 2004 our group hosted another student (Sherrell Turner) with scholarship awarded by BGSU's Academic Investment in Math and Science program, who also received an award from the Glenn Stokes Summer Research Internship. Both of these students belonging to an underrepresented group were supervised by the PI's and his graduate students and expressed their excitement and strengthened interest in the chemistry, and in science in general.

Mr. Cesar Perez (left) and Ms. Sherrell Turner enjoying their hands-on experience in the PI's laboratory.