Characterization of metal-functionalized flax orbitide as a new candidate for light-emitting semiconductor

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Abstract. Organic materials display promise in numerous electronic applications, complimentary to traditional semi-conducting materials. Cyclolinopeptides show promise in light-emitting applications as an organic semiconductor. Photoluminescence measurements indicate charge transfer between the peptide and the metal, resulting in an increase in intensity of the emission from around the metal in the Cyclolinopeptide complex. Complementary X-ray absorption near-edge spectroscopy (XANES) shows a change in occupation of energy states in the peptide when complexed with the metal, indicating charge transfer, but peak positions show the peptide is not chemically changed by the metal. Combining X-ray emission and XANES provides element specific partial density of states, to estimate the element specific energy gap which is the proposed emission range for the peptide material. Organic light emitting diode devices have been fabricated, although no measurable emission has been seen as of yet. The devices have diode like current-voltage characteristics showing the peptide is semi-conducting with a threshold voltage of approximately 2.5 V.

1. Introduction

Organic electronics is a growing field driven by the low cost of fabrication and innate flexibility of organic materials. The cost reductions arise from the roll to roll processing, or printing fabrication potential of organic materials [1]. These methods reduce the amount of material utilized by employing bottom up fabrication, instead of the top down fabrication currently employed for mass produced electronics. The characteristics of the active organic material result from the chemical structure of the organic molecules rather than the dopant atoms in a silicon lattice, thereby eradicating the need for ion implantation of the active material. The vast number of suitable organic molecules and the potential for engineering their electronic properties, providing an almost endless supply of organic materials to be tested for electronic applications.
Cyclolinopeptides (CLs) are naturally occurring cyclic, hydrophobic and biologically active orbitides found in flaxseed, flax roots and flaxseed products [2, 3]. This group of orbitides comprise 8 or 9 proteinogenic amino acids fused at terminal amino and carboxyl groups to form stable cyclic structures [2]. The geometric arrangement of the atoms in the ring structures is greatly affected by environmental considerations, as well as functionalization and metal complexes. The effect of these considerations is a change in the twisting of the CL structure as seen by looking at the crystal structure, which is affected by the solvent from which the crystal was grown [4].

For photon emission from organic materials one must first look at the exciton (excited electron-hole pair) which undergoes recombination resulting in light emission. There are two main types of exciton pairs that are generally considered in emission of visible light from organic materials: singlet state, and triplet state excitons [5]. The difference between the two types of excited states is that a triplet state has a net electron spin of one and a singlet state has a net electronic spin of zero. This results from the orientation and phase of the spin of the excited electron with respect to its counterpart in the ground state. If the spin orientation or phase is the same for both excited and ground state electrons of the exciton then this is a triplet state, otherwise it is a singlet state exciton. Singlet state emission (fluorescence) is much more rapid because the transition does not require a change of spin orientation or phase of the electron. Triplet state emission (phosphorescence) is much slower and tends to result in a glow even after the device is turned off due to the lower probability of recombination of triplet state excitons [6].

Generally in organic electronics one can expect approximately 75% triplet state excitons and 25% singlet state excitons [7]. This causes the efficiency of emission from singlet state focused devices to suffer by limiting the proportion of singlet carriers, but benefits devices focused on triplet state emission [8]. This may be accomplished by adding a heavy atom (such as terbium (Tb) or europium (Eu)) to the system, which is a known method to enhance triplet state emission in organic systems. Organic materials have weak spin-orbital interaction because they are made up of materials that do not have a bound \( d \)-state. The heavy atom has larger spin orbit interaction of the system because they have a bound \( d \)-state and the spin orbit interaction is generally seen in the interaction between the \( p \)-states and partially occupied \( d \)-states of transition metals.

Transition of triplet state excitons to singlet state excitons at metal sites creates localized sources of singlet excitons, increasing the exciton emission in the organic metal complexes; that could then cause a cascade of emission via stimulated emission [9].

2. Experiments and Discussion

Three techniques were employed to characterize CLs: photoluminescence (PL), XANES, X-ray emission spectroscopy (XES), and current-voltage (I-V) characterization of organic light emitting diode (OLED) devices. PL measurements used a 240 nm ultraviolet light source and an Ocean Optics QE65000 spectrometer. XANES and XES spectra of carbon, oxygen, and nitrogen \( K \)-edge absorption and non-resonant \( K \)-\( \alpha \) emission respectively, were collected at the Resonant Elastic and Inelastic X-ray Scattering (REIXS) beam line at the Canadian Light Source (CLS). OLEDs were fabricated using a standard four layer device structure. The four-layers are an emissive layer, a buffer layer, front and back electrodes. The front and back electrodes were indium tin oxide (ITO) and gold respectively. CLs complexed with various transition metals are used as the emissive layer. Between the front electrode and emissive layer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is employed as a buffer. I-V characterization of OLEDs were performed using a Keithley 2420 source measure unit.

PL measurements have been used to examine the emission properties of various CLs, containing several different transition metals. One such system is shown in Fig. 1 where one can see the change in the PL spectrum of Tb when it is complexed with cyclolinopeptide D (CLD). The orbitide CLD was chosen for this investigation because it contains tryptophan as one of the
amino acids in the peptide structure; tryptophan is an excellent absorber of short wavelength electromagnetic radiation. Looking at Fig. 1 one can see the reflected UV light in the 240 nm region, with a large reflected peak in the Tb sample; when CL is added the reflected peak is greatly reduced. The reduction in reflected peak intensity is likely caused by absorption by the tryptophan in the CLD structure, but could also be caused by scattering in the CLD structure. Absorption is most likely due to the enhanced emission from Tb sites observed. Tryptophan also has an emission band in the 250-300 nm region, which does not appear in the collected spectrum, indicating charge transfer being the mechanism for energy transfer to the Tb rather than a secondary emission-absorption process. These interpretations are supported by looking at the interaction of Tb and Eu in other CL structures using XANES.

![Figure 1: UV excited PL measurements of Tb and CLD Tb complex, showing enhancement of emission with CLD present indicating charge transfer.](image1)

![Figure 2: Nitrogen K-edge XAS of CLB and metal complexes, indicating chemical stability of CL and charge transfer in change in state occupation.](image2)

![Figure 3: Carbon K-edge XES (left) and XAS (right) spectra to estimate element specific energy gap of in CLD Tb complex](image3)

![Figure 4: CLD terbium complex I-V characterization in runs of 4 successive tests, showing change in line shape.](image4)

Carbon and nitrogen K-edge XANES spectra (Fig. 2) indicate a change in the occupation of localized energy states attributed to bonding in the organic molecule. The energy location of peaks in Fig. 2 does not change between samples, meaning the chemical structure of the molecule is unchanged by metal addition to the system. The change in state occupation, seen as the variation in peak intensity, indicates charge transfer between the metal and CL. Combining the XANES and XES yields the element specific partial density of states as shown in Fig. 3; the element specific energy gap is estimated to get an idea of the maximum possible emission...
energy of 2.9 eV for the CLD.

I-V characterization of OLED devices was done to look at the turn on potential and relate emission to current. The I-V curves from one device provide the threshold voltage of approximately 2.5 V, even though no emission has been observed (Fig. 4). I-V characteristics show the typical diode line shape for the first run but subsequent runs immediately following show a significant change in the line shape. The line shape returns to its original shape after some time but changes again after the first run of the test, indicating a possible saturation of states resulting in a more conductive electronic structure.

3. Summary
In summary CLs are cyclic hydrophobic orbitides that occur in flax and show promise as light emitting materials. Charge transfer between CLD and a complexed metal was revealed by enhanced emission from the metal site under UV irradiation. This is supported by XANES measurements where intensity changes indicate a change in the occupation of states in the presence of the metal, while the peak positions remain unchanged indicating chemical stability. The enhanced emission indicates a possibility to utilize the plentiful triplet state excitons in organic materials for light emission.

Element specific energy gap estimation finds a maximum possible energy gap value (energy of emitted light) of 2.9 eV for CLD. OLED fabrication shows the semiconducting nature of CLD and a threshold voltage for devices made from CLD of approximately 2.5 V. There is a change in the line shape of I-V characteristic after the first test, but a return to a diode shape occurs when the system relaxes. The ability to tailor CLs for OLEDs by complexing with metals can be used to improve the performance of the devices for light emission, making CL-metal systems diverse and promising for OLED applications.

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