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COORDINATION-POLYMER FILMS BY REACTIVE SELF-ASSEMBLY

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Abstract: A novel self-assembly technique for the growth of insoluble and intractable thin organic films is presently reported. Bifunctional 8,8'-dihydroxy-5,5'-biquinoline (bisquinoline) is reactively self-assembled with diethyl zinc to form a linear coordination polymer. FTIR, UV/VIS spectroscopy, profilometry, and photoluminescence measurements were used to characterize these new multilayer films. The growth of these films on glass substrates was monitored by increasing absorbance at 396.6 nm using UV/VIS spectroscopy and by profilometry. FTIR spectroscopy indicated that the self-assembled films are polymeric in nature. The reduction of end-group hydroxyls and a significant red-shift of the photoluminescence emission spectrum with respect to zinc bisquinoline powder was attributed to an increase in conjugation length.

INTRODUCTION

Considerable research efforts from both industry and academia have been directed toward the development of new methodologies in fabricating ultra-thin organic/polymeric films of controlled architecture, high processability and robustness (Ref. 1). Incorporation of these films in optoelectronic applications (such as light emitting diodes (LEDs)) impose additional requirements including semiconductor purity and stringent dimensional control (Ref. 2). Thermal evaporation of small molecules and oligomers has led to significant advances in film uniformity and architectural control (Refs. 3-5). However, their performance in applications having elevated temperatures is limited by morphological changes (Refs. 6-9). Polymers have been proposed to overcome such problems of structural stability (Refs. 10,11), but come with compromised purity because of the inability to purify long molecules with defects incorporated on their chains (Refs. 12, 13).

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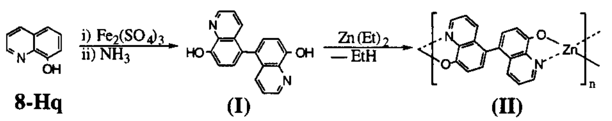
Supramolecular and local structure of thin organic films has been pursued also by self-assembly. Polymers as well as small molecules have been self-assembled to yield uniform thin-films for semiconductor applications (Refs. 14-19). Poly(anions) with poly(cations) encompass current polymer self-assembly techniques (Refs. 15-17,20). Precise film growth from small molecules has been achieved by self-assembly of zirconium organo-phosphonates (Ref. 14,18,21), cobalt-diisocyanobenzenes (Ref. 22), ruthenium pyrazines (Ref. 19), and ω-mercaptoalkanoic acids with copper or gold (Ref. 23).

The quest for polymer analogs of 8-hydroxyquinoline-based metal chelates (such as Alq_3, etc.) for electroluminescence applications has been a challenging task. These metal chelate polymers are nontraditional polymers and are usually associated with considerable handling difficulties. Their major intricacy arises from complexation-decomplexation dynamics, which are very sensitive to the pH and ionic strength of the solute (Ref. 24). For linear metal chelate polymers, solubilization typically occurs only in polar aprotic solvents (Ref. 25), which are difficult to remove from spun films. The insoluble and intractable nature of these polymers makes them amenable to the self-assembly growth which is the subject of this paper.

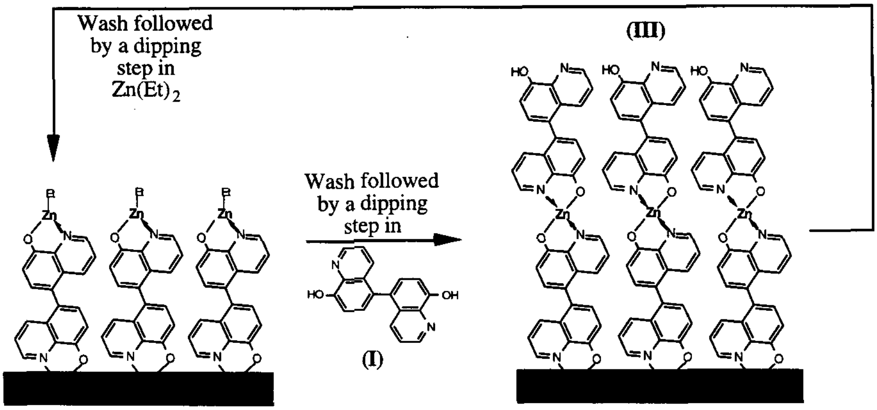
RESULTS AND DISCUSSION

Coordination polymers based on quinoline chelates were studied extensively in the early 1960s by Philips *et* al. (Ref. 23), and by Berg *et* al. (Ref. 25). The chelation of zinc and other divalent cations with bisquinoline **(I)** was shown to be an 1:1 metal/ligand ratio (see Scheme 1). The good thermal stability of such compounds stimulated additional investigation by Archer *et* al. (Ref. 26). On the other hand, processing difficulties were demonstrated with reduced solubility and purification of bisquinoline derivatives and related metal chelates. The introduction of high-vacuum sublimation of bisquinoline **(I)** along with the reactive nature of diethyl zinc in dilute solutions of **(I)** resulted insoluble oligomers of poly(Zn-bisquinoline) **(II)** of high purity (see Scheme 1).



Scheme 1. Synthesis of bisquinoline **(I)** and its zinc-chelate polymer **(II)**

The natural limitations of the solution polymerization were circumvented by sequential layering of the polymer repeat units based on a reactive self-assembled motif (see Scheme 2). Self-assembled polymeric Zn-bisquinoline films were grown on hydroxy-functionalized glass, and silicon substrates. Highly pure $Zn(Et)_2$ and bisquinoline were diluted to 10^{-3} and 10^{-5} M in dry THF. Coating was initiated by dipping first into a THF solution of $Zn(Et)_2$. This is followed by a rinse in the THF bath (which is constantly refluxed and circulated over Na), followed by dipping in a THF solution of bisquinoline. Both dips were limited to equal times of one to two minutes. The layer thickness progressively increased by repeated cycling through the dipping sequence (see Figure 1).



Scheme 2. Methodology for growing poly(Zn-bisquinoline) (III) via reactive self-assembly.

The insoluble and intractable nature (Ref. 27) of **(II)** has been crucial in the fabrication of this polymer by self-assembly. The layered film growth by repeated cycling through the dipping sequence was confirmed by the steady increase in absorbance due to the formation of zinc-bisquinoline (UV maximum at 396.6 nm, see Figure 1). The film thickness also increased as measured by profilometry. Superb film uniformity was readily achieved over the entire dipped substrate and no major scattering from large film inhomogeneities was observed. The UV/VIS and film thickness measurements showed that the layering efficiency increased after four dipping cycles. This could be attributed to initial anchoring difficulties on the substrate surface. The thickness of the layers versus dipping cycles showed that the layers do not necessarily increase by one zinc-bisquinoline repeat unit per layer but possibly as dimers or trimers. These oligomeric species (presumably formed by incomplete rinsing) could also be utilized for speedier film growth, ranging from 10-30 Å layers (monomer to trimer) per cycle. This reduced the construction of a 1 200 Å film to about 2.7 hours with the increased layering versus the 8 hours originally anticipated.

Figure 2(a) and 2(b) illustrates the FTIR spectra of bisquinoline **(I)** and zinc bisquinoline powder **(II)**, respectively. Evidence of chelation is shown by comparing the

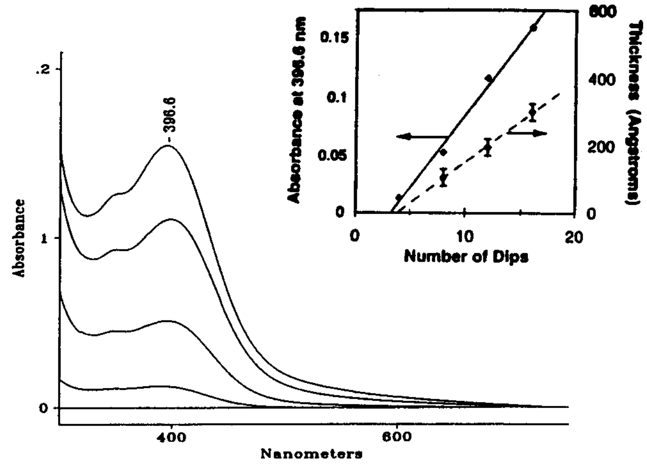


Fig. 1. UV/VIS absorption vs. number of complete dip cycles. Inset depicts the film thickness and absorbance at 396.6 nm.

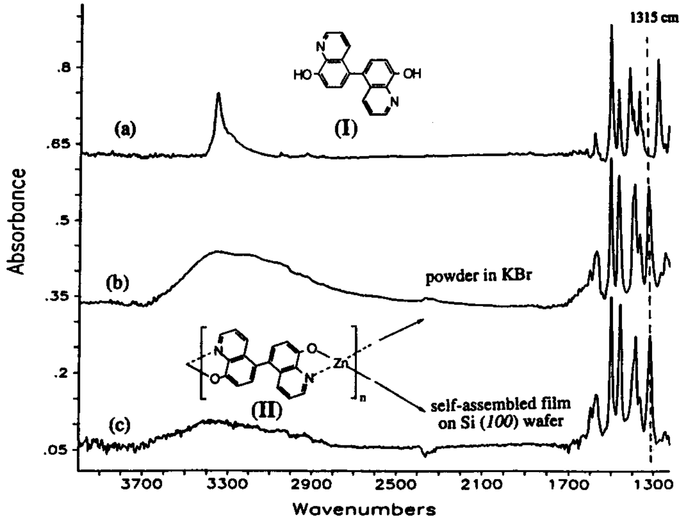


Fig. 2. FTIR spectra of (a) bisquinoline (I) in KBr, (b) powder form of poly(Zn-bisquinoline) (II) in KBr and (c) self-assembled film of (III) on a (*100*) silicon wafer.

changes in vibrational frequencies of (I) with the powder (II) and the self-assembly (III). The FTIR of zinc-bisquinoline (III) layered on a silicon wafer was compared to powdered samples of bisquinoline (I) and zinc-bisquinoline (II) and showed a noticeable decrease in the broad hydroxyl stretch at 3400 cm^{-1} (see Figure 2). This decrease was attributed to disappearance of terminal hydroxyl groups that strongly absorb at 3355 cm^{-1} for the unchelated bisquinoline (free OH stretch) versus the broad OH band (hydrogen-bonded OH stretch) based on terminal end-groups. The peak at 1315 cm^{-1} which is indicative of chelation in the layer assembly (III) is present in the powder sample (II) as well, but is not present in unchelated bisquinoline (I). Bisquinoline (I) has a peak at 1285 cm^{-1} for a phenolic C-O stretch, not found in the chelated samples. The FTIR spectra provide sufficient evidence that chelation is the primary mechanism contributing to self-assembly.

The photoluminescence (PL) of the zinc-bisquinoline molecular assembly on a silicon wafer shows a broad emission centered at 590 nm (see Figure 3) This spectrum is significantly red-shifted with respect to the zinc bis-(8-hydroxyquinoline) (Znq_2) photoluminescence emission spectrum which has a sharper emission maximum at 518nm. This is attributed to the increased conjugation for the coordination polymer versus its low molecular weight analog of Znq_2. The difference in conjugation length between the precipitated zinc-bisquinoline powder (II) and self-assembled films of (III) is further demonstrated in Figure 4. The red-shifted shoulder in the PL emission of (II) is indicative to the significant lower conjugation of that from the self-assembled films of (III).

The insoluble and intractable nature of these chelates, along with their improved processability, film forming quality and increased purity enables their usage in a variety of semiconducting applications (Ref. 27).

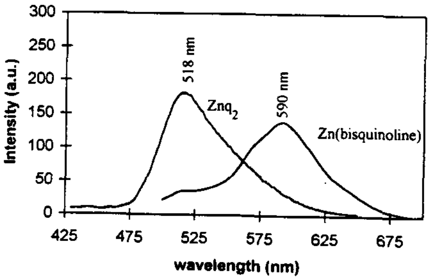


Fig. 3. PL spectra of molecular zinc-bis-(8-hydroxyquinoline powder and zinc-bisquinoline (III) self-assembled on a silicon wafer.

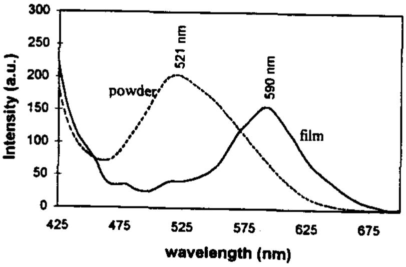


Fig. 4. PL spectra of zinc-bisquinoline powder (II) and self-assembled film (III) on a silicon wafer.

EXPERIMENTAL

Instrumentation Room temperature ^{1}H NMR was performed on a Bruker 500 MHz spectrometer. FTIR was performed on a Nicolet 60sx instrument using a DTGS detector. 32 scans were accumulated at 4 cm^{-1} resolution. 1% KBr powder samples of bisquinoline **(I)** and zinc-bisquinoline **(II)** pellets were used. Double polished silicon *(100)* wafer was utilized to grow self-assembled zinc-bisquinoline **(III)**. These substrates were transparent above 1200 cm^{-1}, and their spectra were taken by orienting them at 45° angle with respect to the incident beam to minimize thickness induced interference fringes. (See Figure 2)

UV/VIS Absorption Spectroscopy of **(III)** on glass was performed on a Perkin-Elmer UV/VIS/NIR Spectrophotometer Lambda 900. Spectra were collected from 750-250 nm with an interval of -0.50 nm at speed of 250 nm/min.

The photoluminescence (PL) emission spectra were done using a Perkin Elmer LS50B. A zinc-bisquinoline molecular assembly on a silicon *(100)* wafer was done with an excitation wavelength of 400nm, 100nm/min scan rate, 10nm excitation slit width, and 20nm emission slit width. The PL of powder zinc bis (8-hydroxyquinoline) (Znq_2) and powder zinc-bisquinoline in a KBr pellet were recorded with a 400nm excitation wavelength.

Film thicknesses were determined using a Tencor Alpha Step 200 after scratching the slides with a fresh razor. Measurements for **(III)** on silicon and glass were done with a 10 mg weighted stylus for 400 mm sweep at 8 s scan.

Monomer Synthesis The synthesis of bisquinoline **(I)** was done following the method of Archer *et* al.(Ref.26) Prior to its use, it was purified by sublimation. The compound was a white powder with a m.p. 280-300 °C (dec.). The room temperature ^{1}H-NMR spectrum of **(I)** in d^6-DMSO showed peaks (ppm) at 9.98(br s, 2H, OH), 8.87(d, 2H, J = 2.77 Hz), 7.64(d, 2H, J = 8.24 Hz), 7.42(m, 4H), and 7.21(d, 2H, J = 7.75 Hz). The FTIR of **(I)** is shown if Figure 2(a).

Zinc-Bisquinoline Powder Preparation Zinc-bisquinoline powder **(II)** was prepared by adding 1:1 equiv. of bisquinoline (0.347 mmole) and $ZnCl_2$ in a 10 ml glacial acetic acid, 10 ml concentrated HCl, and 10 ml distilled water and then adding 4 M ammonia dropwise until precipitation occurred at pH 3.5. The powder was collected via gravity filtration, washed with distilled water, and then vacuum dried overnight at 56 °C to produce a 100% yield. It was then soxhlet extracted overnight in THF and vacuum dried at 56 °C for three hours, ending up with a 75% yield. FTIR is shown in Figure 2(b) .

Polymer Synthesis by Self Assembly $Zn(Et)_2$ was purchased from Aldrich. THF was purchased from J.T. Baker and refluxed over Na with benzophenone under nitrogen and distilled. Glass and quartz substrates were hydroxy-functionalized according to the method described elsewhere (Ref.15). Silicon substrates were hydroxy-functionalized with concentrated NaOH solution, washed with distilled water, and air dried.

Solutions of bisquinoline and $Zn(Et)_2$ were made from THF at 10^{-5} to 10^{-3} molar concentration . Hydroxy-functionalized surfaces were first dipped in the $Zn(Et)_2$ solution for one to two minutes, followed by a rinse in the THF bath for an equal amount of time. The substrate was then dipped into the bisquinoline solution for one to two minutes followed by another THF rinse to form a polymer repeat unit of zinc-bisquinoline. In this fashion, the film thickness increases by cycling through the dipping sequence.

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