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Highly Efficient Solid-State Electrochemically Generated Chemiluminescence from Ester-Substituted Trisbipyridineruthenium(II)-Based Polymers

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Abstract: A polymerizable ester-substituted trisbipyridine complex of ruthenium(II) has been synthesized and the solid-state electrochemiluminescence (ECL) properties of its polymer evaluated. A collection of 12 "sandwich-type" solid-state cells were investigated each having a ∼0.3 μm thick film of the polymer sandwiched between a transparent indium/tin oxide (ITO) anode and a porous Au cathode. The ECL of these devices was evaluated in the solid state. Despite considerable variability in performance, the most efficient of these devices exhibited ECL quantum yields matching the efficiency of the best organic polymer based light-emitting devices.

Introduction

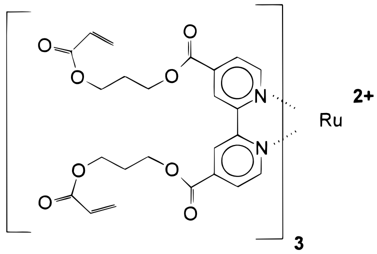
The complex tris(bipyridine)ruthenium(II) is remarkably photoluminescent in solution having an emission quantum yield, Φ_E, in the range of 7% in dry acetonitrile.[1] This complex also exhibits electrochemically generated luminescence (ECL) in dilute solution via the reaction[2]

$$\mathrm{RuL_3}^{3+} + \mathrm{RuL_3}^{1+} \rightarrow \mathrm{RuL_3}^{2+} + \mathrm{RuL_3}^{2+*} \rightarrow 2\mathrm{RuL_3}^{2+} + h\nu \qquad (1)$$

Moreover, in acetonitrile solution the quantum efficiency for ECL emission, Φ_{ECL}, is 5%—only modestly smaller than Φ_E under similar conditions.[2]

More recently ECL has been observed in the solid state from electrochemically formed films of poly-Ru(vbpy)$_3$, where vbpy is 4-vinyl-4′-methyl-2,2′-bipyridine.[3,4] The most successful of these studies, at least in terms of emission stability, has involved a dual electrode arrangement employing an interdigitated array electrode (IDA) where the polymer spans the gap (<5 μm) separating the "fingers" of the two electrodes.[4] In this configuration when appropriate voltages are applied, oxidation of $\mathrm{RuL_3}^{2+}$ will ensue at one electrode and reduction at the other. At steady state, time-independent gradients of $\mathrm{RuL_3}^{3+}$ and $\mathrm{RuL_3}^{1+}$ are established in the polymer. At the interface of these two gradients the light-emitting reaction depicted in (1) occurs. Furthermore, the electrochemical process which generates $\mathrm{RuL_3}^{3+}$ and $\mathrm{RuL_3}^{1+}$ is a disproportionation reaction that is overall charge neutral—i.e., the reaction requires no charge compensating ions to enter or leave the polymer. Consequently, such assemblies can be operated entirely in the solid state (i.e., in the absence of electrolyte solution), vide infra. While devices based on poly-Ru(vbpy)$_3$ have been demonstrated to exhibit good reproducibility and light emission stability, Φ_{ECL} has proven to be meager (≈0.03%).[4]

Tris(2,2′-bipyridine)ruthenium(II) complexes in which the bipyridines are substituted in the 4- and 4′-positions with −COOR functions exhibit significantly enhanced solution photoluminescence when compared with the unsubstituted analogue. For example, in O$_2$-free acetonitrile at room temperature the ethyl ester-substituted complex has $\Phi_E \approx 30\%$.[5] Additionally, these electron-withdrawing ester functions shift, in the positive direction, E′°(3+/2+) by ∼300 mV and E′°(2+/1+) by ∼380 mV.[6] Given the very high quantum efficiency for photoluminescence of the ethyl ester complex, we have prepared a polymerizable analogue, **I**, in an effort to determine if ester substitution in the 4- and 4′-positions of the bipyridine ligands also results in high quantum efficiencies for solid-state ECL. As reported herein, we find that the ECL efficiencies of polymer films of **I** are substantially better than other tris(bipyridine)ruthenium-based ECL systems previously studied and are comparable with the best organic LED's available.



I

Results and Discussion

Synthetic details for the preparation of **I** and the corresponding ligand are given in the Experimental Section; however, they follow closely the procedure for preparing the 5,5′-substituted analogue reported previously.[7] In acetonitrile solution **I** exhibits electrochemistry ($E'°$(3+/2+) and $E'°$(2+/1+)) and photo-

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luminescence (Φ_E) virtually identical to the ethyl ester-substituted complex.[5,6] Unlike Ru(vbpy)$_3$, **I** shows no tendency to polymerize electrochemically. Rather, **I**, as the PF_6^- salt, can be cast from acetonitrile solution (spin-, dip-, or spread-coated) to form uniform glassy films when dry. These films can be polymerized thermally (150 °C, ≥1 h) or photochemically (UV), yielding robust, electroactive films.

A group of 12 so-called "sandwich-cell" devices were fabricated from **I** as described in the Experimental Section. Briefly, these cells consist of an ~0.3 μm film of poly-**I** sandwiched between an optically transparent indium/tin oxide coated glass (ITO) anode and a porous gold "minigrid" mesh cathode (2000 lines/inch, Buckbee-Mears, St Paul, MN). To initiate the ECL reaction and establish the steady-state redox site gradients within the polymer film, each sandwich cell was first exposed to acetonitrile-saturated N_2 in a vial stoppered with a septum through which the electrode leads passed. A voltage bias of 2.5 V was imposed between the Au cathode and ITO anode. Within a few seconds of applying the bias, visible luminescence was typically evident through the ITO electrode. The assembly was removed from the vial inside of an inert atmosphere box and allowed to dry under bias. As the polymer dried (over a period of ~5 min) the current decreased, finally stabilizing at a value typically one-tenth that of the current initially observed with the polymer fully solvent swollen. Concomitantly with the decrease in current, the light emission diminished.

The ECL emission of each fully dried assembly was measured (Center for Advanced Multifunctional Polymers and Molecular Assemblies, University of Arizona, Tucson, AZ) from the ITO side using a silicon photodetector mounted in a special housing calibrated to measure the external emission quantum yield. *External* and *internal* emission quantum yields (or efficiencies) differ in that the former is the number of photons escaping the front surface of the device per electron passed while the latter is the total number of photons generated per electron passed. Of the 12 devices investigated 6 emitted below the measurement threshold of the silicon detector although all 12 were visibly emissive to the eye. For the remaining 6 devices each behaved in qualitatively similar fashion; however, there was considerable variation in resistance and *external* Φ_{ECL}. Current densities at 5.0 V bias ranged from 1 to 29 mA/cm^2 and external Φ_{ECL} ranged from 0.06% to 0.92%. By comparison with devices of similar construction and known *internal* quantum efficiency, it is estimated that the *internal* quantum efficiencies of the present devices is 4−6 times larger than the *external* efficiency directly measured.[8] Consequently, for the most efficient of the devices tested the internal Φ_{ECL} should be ~4.5%. Figures 1−3 present data obtained from this most efficient device.

Figure 1 is a plot of the current density (mA/cm^2) and luminance (cd/m^2) vs bias voltage. Figure 2 is a plot of external Φ_{ECL} vs bias voltage calculated from the data in Figure 1. Both the emission intensity and current increase approximately monotonically with bias voltage above ~2.5 V. The quantum efficiency is maximized at ~5 V and decreases slightly at higher bias voltages. When these devices are operated at bias voltages ≥10 V there is a noticeable decay of emission with time which accelerates as the voltage is increased.

Figure 3 is a plot of emission intensity and current density vs time for the same device as in Figures 1 and 2 after, first, removing the bias voltage for 5 min and then reapplying a 5 V bias at $t = 0$. After roughly 2 min the current and emission recovered and reached steady values which exhibited minimal decay after ~9 min of operation.[9] This result also serves to illustrates that, at room temperature, there is very limited

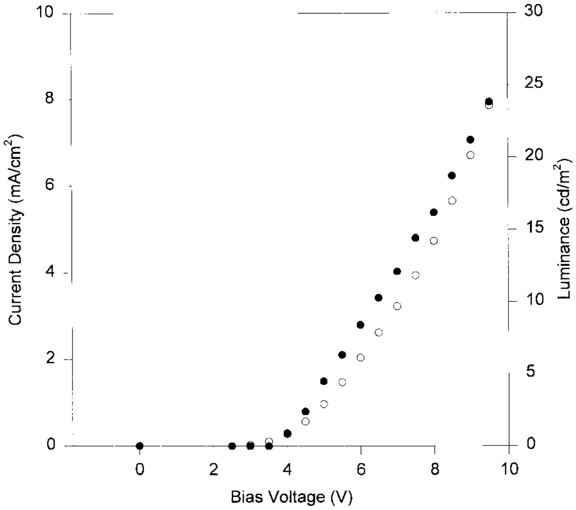

Figure 1. Current density (open circles) and luminance (solid circles) vs bias voltage for a poly-**I**-based sandwich cell (see text).

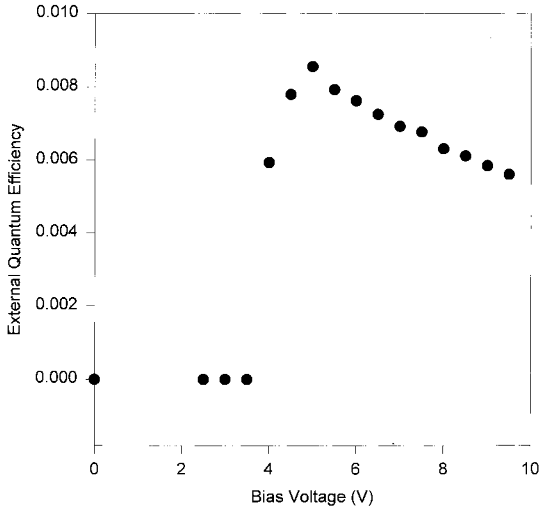

Figure 2. External quantum efficiency vs bias voltage for the same cell as Figure 1.

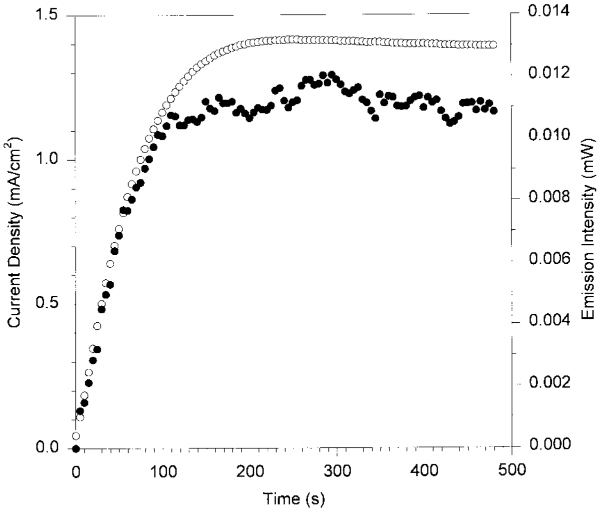

Figure 3. Current density (open circles) and emission intensity (closed circles) as a function of time after application of a 5.0 V bias (see text) to the same cell as in Figure 1.

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counterion mobility within this material when dry. For example, once the redox concentration gradient is established in a solvent-swollen film and the polymer dried, the bias voltage can be removed and reapplied after ~24 h and visible ECL emission typically reappears within 5−10 min.

The considerable variability in the ECL efficiency of these cells from device to device most certainly arises from their rather primitive design and construction. That point notwithstanding, the performance of the most efficient device demonstrates that at a minimum with proper engineering, internal $\Phi_{ECL} > 4\%$ are attainable with polymers of **I**. This level of efficiency is 20 times greater than the next highest efficiency of which we are aware for a RuL$_3$-based pure ECL solid state device (vide infra).[4,10] Moreover, it is unlikely that the specific result reported herein represents the maximum efficiency possible from an optimized device based on this polymer system—it, rather, represents a lower limit to what might be possible. Preliminary experiments with IDA electrodes coated with poly-**I** in contact with solution electrolyte have been conducted which suggest even higher efficiencies should be attainable.[11] In the IDA configuration ECL results from film to film are, thus far, considerably less variable than for the solid-state sandwich devices. On the other hand, the ECL emission is less stable, typically lasting only a few minutes. Nonetheless, results from IDA experiments indicate that internal Φ_{ECL} values between 7% and 10% are possible with poly-**I** under certain conditions.

Finally, the mechanism by which charge is injected into poly-**I** is entirely electrochemical—that is, it is as we have defined it above, a "pure" ECL system. As such, the number of oxidized charge carriers (Ru^{3+}, "holes") and reduced charge carriers (Ru^{1+}, "electrons") injected per unit time must exactly match. Therefore, were it not for nonradiative processes, the material should exhibit a 100% ECL internal quantum efficiency (i.e., one photon/electron). For so-called electroluminescent materials (EL) such as poly-*p*-phenylenevinylene charge injection is nonelectrochemical and thus there is no a priori requirement that the flux of holes and electrons match. Here the minority carriers are the "limiting reagent" in the light-emitting reaction and their flux determines the maximum number of excited states generated per unit current. Nonradiative processes notwithstanding, pure ECL systems should, in principle, be inherently more efficient than pure EL systems. In practice, prior to the present study, RuL$_3$-based pure ECL materials have not exhibited efficiencies which compare particularly favorably with the better EL materials. Recently several reports have appeared on RuL$_3$-based materials which exhibit mixed modes of charge injection.[12,13] These materials have characteristics intermediate between those of either of pure-mode materials (i.e., ECL and EL).[14] In several instances *very* high external quantum efficiencies (1−3%) were reported.[12] These results are truly remarkable in that, in some instances at least, the internal electroluminescent quantum yields implied by the reported external quantum yields[8] significantly exceed the solution photoluminescence quantum yields for the same lumophore.[12]

Experimental Section

4,4′-Bis[(3-acrylylpropoxy)carbonyl]-2,2′-bipyridine (DEAB). 4,4′-Dicarboxy-2,2′-bipyridine was prepared from 4,4′-dimethyl-2,2′-bipyridine (DMB, Reilley Industries, Indianapolis, IN) following the procedure described by Oki and Morgan.[15] The carboxylic acid was converted to the acid chloride by refluxing 4 g of finely ground acid in 150 mL of thionyl chloride under nitrogen for 6−12 h or until the solution became essentially clear. Excess thionyl chloride was removed by rotoevaporation. To minimize hydrolysis by atmospheric moisture, the crude acid chloride was immediately converted to the bis-1,3-propanediol ester.

Typically, 60 mL of 1,3-propanediol was added to ~4 g of the diacid chloride dissolved in 300 mL of dichloromethane. This solution was heated to reflux for 1 h, cooled to room temperature, and extracted four times with 0.2 M aqueous sodium carbonate to remove excess diol. The dichloromethane layer, containing the intermediate product, 4,4′-bis[(3-hydroxypropoxy)carbonyl]-2,2′-bipyridine, was brought to dryness by rotoevaporation and the solid redissolved in a mixture of 300 mL of acetonitrile containing a large excess of acryloyl chloride. This solution was refluxed for 45 min, and then the solvent was removed by rotoevaporation. The resulting thick liquid was diluted with 75 mL of 5% v/v triethylamine in water. This solution was extracted four times with dichloromethane, and the organic fractions were combined and dried over sodium sulfate before being evaporated to dryness. During the course of the reaction ~10% of the acrylate vinyl groups are hydrochlorinated by HCl produced in the reaction. To reverse this reaction the crude product was refluxed under nitrogen in a 5% v/v solution of triethylamine in dichloromethane for 4 h. Finally, the DEAB ligand was chromatographed (silica, 1:3 acetone/dichloromethane) giving the product in 60% overall yield. ^{1}H NMR (δ in ppm from TMS in CDCl$_3$, multiplicity, integration): 2.2 (q, 2H); 4.3 (t, 2H); 4.5 (t, 2H); 5.8 (d, 1H); 6.1 (d of d, 1H); 6.4 (d, 1H); 7.9 (d, 1H); 8.8 (d, 1H); 8.9 (s, 1H).

[Ru(DEAB)$_3$](PF$_6$)$_2$, I. Ru(DMSO)$_4$Cl$_2$ (162 mg) was dissolved in ~30 mL of ethylene glycol and heated to reflux until an orange color developed. This solution was cooled to 120 °C whereupon 4.2 equiv (685 mg) of the DEAB ligand was added. After 2 h at this temperature, the solution was cooled to room temperature, diluted with 150 mL of water, and a few milliliters of saturated aqueous NH$_4$PF$_6$ were added. The orange precipitate was collected by filtration and chromatographed on silica eluting with acetonitrile. Three bands, each of which contained a trisbipyridineruthenium complex, resulted: **a** (rf = 0.9), **b** (rf = 0.5), and **c** (rf = 0.1). All had identical visible spectra and all fluoresced under long wavelength UV light. The ^{1}H NMR spectra of each was very similar; however, the integration for the acrylate protons was slightly less than expected in the case of **b** and **c**. In addition, no peak in the electrospray mass spectrum of either **b** or **c** could be matched with fragments from the anticipated structure. The ^{1}H NMR, mass spectrum, and chromatographic retention times all suggest that **b** and **c** are quite likely the dimer and trimer, respectively, of the monomer, **a**. The fraction containing **a** was reduced in volume to 10 mL and added to 60 mL of diethyl ether, whereupon the complex precipitated as a fine powder. The solid was collected by centrifugation, washed with diethyl ether, and redissolved in acetonitrile. This solution was stored at −20 °C and was used for casting films of **I**. Yield of component **a** was 35%. ^{1}H NMR (δ in ppm from TMS in CDCl$_3$, multiplicity, integration): 2.2 (m, 2H); 4.3 (t, 2H); 4.5 (t, 2H); 5.8 (d, 1H); 6.1 (d of d, 1H); 6.4 (d, 1H); 8.0 (m, 2H); 9.0 (s, 1H). Electrospray MS: $m/z = 753.2$. UV−visible (wavelength in nm, ϵ/ϵ_{MLCT}): 226 (2.7); 244 (1.3); 308 (3.1); 354 (0.7); 436 (0.7); 466 (1).

ECL Sandwich-Cell Preparation. The anode of each sandwich cell consisted of a rectangular piece (~2×1 cm^2) of indium/tin oxide (ITO) coated glass (resistance 300 Ω/square). Each ITO electrode was cleaned by successive sonications in acetonitrile and ethanol, followed by gently swabbing the surface with a dichloromethane-soaked cotton swab.

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(9) While quantitative studies have thus far been limited to time scales on the order 10 min (cf. Figure 3), devices have been operated for up to 18 h at 6 V bias without decays in emission that are detectable to the eye.

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(11) Pichot, F. Photoelectrochemical Properties of Ruthenium Trisbipyridine-Based Conducting Polymers. Ph.D. Thesis, Colorado State University, Fort Collins, CO, 1997.

(12) Lee, J.-K.; Yoo, D.; Rubner, M. F. *Chem. Mater*. **1997**, *9*, 1710.

(13) Lee, J.-K.; Yoo, D.; Handy, E.; Rubner, M. F. *Appl. Phys. Lett*. **1996**, *69*, 1686.

(14) For example, mixed-mode conductors (see refs 12 and 13) typically emit light with a brief lag time following application of the voltage bias (unlike pure EL materials which emit virtually instantaneously) but more rapidly than pure ECL molecules and without much of the pretreatment required to establish the redox site gradients.

(15) Oki, A. R.; Morgan, R. J. *Synth. Commun*. **1995**, *25*, 4093.

The cleaned ITO electrode was heated for ∼10 s with a heat gun, and 2−3 drops of monomer solution in acetonitrile (∼20 μL, 0.3 M) were deposited onto the ITO surface. The solution was allowed to evaporate slowly under an inverted beaker which resulted in a highly uniform thin film of the monomer. To make electrical contact to the ITO the monomer film was removed from an ∼0.75 cm strip along one edge of the electrode surface with a dichloromethane-soaked cotton swab (vide infra). The film was then polymerized at 150 °C for 1−3 h.

At the junction of the bare ITO and the edge of the polymer film, a thin layer (∼1 mm thick and 5 mm wide) of TorrSeal epoxy resin was applied, slightly overlapping the polymer but leaving a free area of ITO at the very end of the slide. After the epoxy was cured at 70 °C overnight, a rectangular piece of gold mesh (2000 lines per inch, 3−5 μm thick; Buckbee Mears, St Paul, MN) of dimensions slightly narrower than the exposed polymer film was carefully placed on top of the polymer film so that it extended up onto the insulating epoxy layer. This gold mesh served as the cathode and allowed solvent to swell the underlying film. At this point, another drop of monomer solution was deposited at the bottom end of the gold grid. This solution was pulled, by capillary action, into the entire grid. This second monomer layer served as an adhesive between the first polymer layer and the gold minigrid. The monomer was swabbed from the part of the gold surface laying atop the epoxy (for subsequent electrical contact). The assembly was then heated at 150 °C for one additional hour to polymerize the new monomer sufficiently to ensure intimate contact between the gold electrode and the original polymer film. Independent electrical contacts were made to the ITO anode and gold cathode using fine Teflon-insulated copper wires and silver print. After the silver print had thoroughly dried these electrical contacts were buried under a second layer of epoxy to avoid their exposure to solvent. Finally, the entire device was placed in a 70 °C oven overnight.

Conclusion

Solid-state devices fabricated from poly-**I** films are capable of ECL efficiencies (i.e., >4%) which are comparable with the best polymer-based light-emitting devices known to date[16,17] and considerably better than other pure ECL devices based on $\mathrm{RuL_3}$ reported thus far.[4,10] Furthermore, in the solid state they exhibit excellent stability. Preliminary findings suggest, that with improved engineering, solid-state devices based on poly-**I** could be fabricated with internal Φ_{ECL} exceeding 7%.

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