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Metallopolymers

# Temperature- and Voltage-Induced Ligand Rearrangement of a Dynamic Electroluminescent Metallopolymer**

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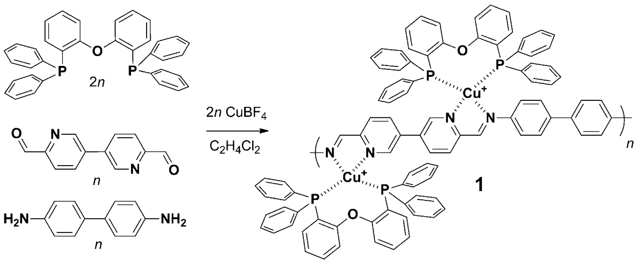
**Abstract:** *A dynamic-covalent metal-containing polymer was synthesized by the condensation of linear diamine and dialdehyde subcomponents around copper(I) templates in the presence of bidentate phosphine ligands. In solution, the red polymers undergo a sol–gel transition upon heating to form a yellow gel, a process that can be either reversible or irreversible depending on the solvent used. When fabricated into a light-emitting electrochemical cell (LEC), the polymer emits infrared light at low voltage. As the voltage is increased, a blue shift in the emission wavelength is observed until yellow light is emitted, a process which is gradually reversed over time upon lowering the voltage. The mechanism underlying these apparently disparate responses is deduced to be due to loss of the copper phosphine complex from the polymer.*

Constitutionally dynamic polymers[1] can reconfigure their structures and properties in response to stimuli in ways that conventional polymers cannot.[2] We report the self-assembly of a dynamic-covalent metallopolymer,[3] which undergoes a reversible structural rearrangement in response to changes in both temperature in solution and electric field in the solid state, transforming its mechanical and photophysical properties. The polymer was formed using the approach of subcomponent self-assembly,[4] in which the condensation of aromatic amine and pyridine aldehyde subcomponents is driven by the preferential coordination of the resulting imines to metal ions. In solution, the polymer showed both thermochromism[5] and "heat-set" gel formation[3c,6] which can be either reversible or irreversible depending on the solvent used.

Furthermore, the polymer was electroluminescent and could be fabricated into light emitting electrochemical cells (LECs), the simplest class of light-emitting devices formed by sandwiching a conjugated polymer containing ionically conductive species between two electrodes.[7] The devices showed voltage-dependent electroluminescence (EL), undergoing a shift in the wavelength of emission that reverses over time. Herein we report the synthesis of metallopolymer **1** and investigate the structural transformation responsible for gel formation as well as the chemical and physical reasons behind the color shift observed in the LEC devices.

Polymer **1** was produced by stirring 6,6′-diformyl-3,3′-bipyridine, benzidine, copper(I) tetrafluoroborate and bis[2-(diphenylphosphino)phenyl]ether (POP) in dichloroethane at 50 °C for 3 h (Scheme 1). The heteroleptic metallopolymer was characterized by $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopy.[3c,8] Diffusion-ordered NMR spectroscopy (DOSY) studies of **1** in dimethyl sulfoxide (DMSO) showed that its diffusion coefficient decreased upon increasing the sample concentration (see Supporting Information, SI, Figure S5). This effect is attributed to the dynamic-covalent nature of the links between the individual repeating units of this dynamic polymer.[9] DOSY studies of the discrete dimeric complex **2**, which was formed using 2-formylpyridine in place of 6,6′-diformyl-3,3′-bipyridine (SI Section S1.3) and is a model for the repeating unit of **1**, indicated that the hydrodynamic radius of the polymer is ca. 3.3 times that of **2** at a concentration of 10.0 g L$^{-1}$ in DMSO (SI Section S2.1.2). Comparison of the residual amine peaks with the newly formed imine peaks indicates a degree of polymerization of approximately seven repeating units (SI Section S2.1.3), which is consistent with the DOSY results and indicates that **1** has an average molecular weight of 12 kDa. The size distribution of **1** was measured by dynamic light scattering (DLS) in DMSO at a concentration of 10.0 g L$^{-1}$, and showed species with sizes in the 10–20 nm range (SI Section 2.2). Larger species were



***Scheme 1.*** Synthesis of polymer **1** from subcomponents.

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observed in the 50–500 nm range and are inferred to be polymer aggregates;[3] these aggregates were also observed by multi-angle static light scattering (SLS) (SI Figure S11).

Polymer **1** dissolved in dimethyl formamide (DMF) to give a deep red solution. The strong absorption peaks observed in the UV/Vis spectra of **1** up to 400 nm were attributed to the $\pi$-$\pi$* transitions of the polymer backbone (N^N) and POP ligands, whereas absorption beyond 400 nm was attributed to the metal-to-ligand charge transfer (MLCT)[16–18] (Figure 1). The polymer has a photoluminescence (PL) maximum at 780 nm, also attributed to the MLCT state. Heating a solution of the polymer (1 wt. %) to temperatures above 160 °C resulted in its transformation to an opaque yellow state which did not flow when its container was inverted, indicating gel formation (Figure 1-inset). The PL spectrum of the gel showed an emission maximum at 580 nm, significantly blue-shifted compared to the polymer solution. The color change, shift in photoluminescence, and gel formation reversed upon cooling the sample to room temperature. This type of reversible gel formation upon temperature rise[4,8–10] is the opposite behavior to that observed for most gelators, which undergo a sol–gel transition upon cooling. We had previously reported a similar effect in a series of related polymers, however, the high temperature of gel formation and poor solubility of the polymers inhibited further study or device fabrication.[3c]

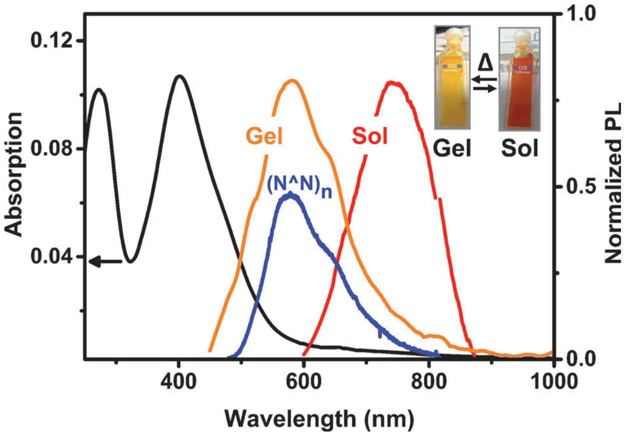

*Figure 1.* UV/Vis absorption (black) and photoluminescence (red) of the polymer **1** in solution and photoluminescence spectrum of the polymer in the gel state (orange). The blue line shows the photoluminescence of the isolated gel matrix. Inset: Photograph showing reversible formation of a yellow gel upon heating a red polymer solution of **1** and the reversible gel forming upon heating.

Heat-set gel formation was also observed to occur in DMSO at lower temperatures than in DMF, allowing the process to be monitored using rheometry. When the sample was heated to 140 °C, the elastic modulus (G′) became an order of magnitude greater than the viscous modulus (G″) and behaved linearly over a wide range of frequencies, indicating gel formation (SI Section S3.1). The DMSO gels remained stable in the rheometer upon cooling to room temperature and were observed to be stable in a vial over several months. Scanning electron microscopy images of the gels showed the formation of fibrous aggregates ca. 10 nm in width and hundreds of micrometers in length (SI Figure S19).

The sol–gel transition was followed in a 1 % [D$_6$]DMSO solution by variable temperature NMR (VT-NMR) spectroscopy in order to elucidate the molecular basis for gelation (SI Section 2.4). The broad $^1$H NMR spectrum of the polymer disappeared upon heating to 90 °C due to gel formation[10] and was replaced by sharp peaks corresponding to those of a [Cu(POP)]$^+$ complex. Comparison with the integrated intensities of peaks from an added adamantane reference indicated total displacement of the [Cu(POP)]$^+$ complex from the polymer upon gel formation. Minimal change was observed in the NMR spectra of the DMSO sample after standing at 25 °C for three days. The transition was further investigated by $^{31}$P NMR and mass spectrometry, which provided data consistent with the liberation of [Cu(POP)]$^+$ upon heating. Similar behavior was observed to occur in DMF by NMR spectroscopy (SI Figure S15). Temperatures greater than 140 °C were required to induce gel formation, and the samples had to be heated outside of the spectrometer and measured rapidly for [Cu(POP)]$^+$ formation to be observed. After leaving the sample to cool to room temperature for 30 min the spectrum had reverted to that of the polymer solution, and after 24 h it matched that of the sample before heating. Repeated heating and cooling of the sample resulted in the gradual build-up of an insoluble yellow precipitate.

The formation of polymer **1** was driven by the tendency of copper(I) to form heteroleptic complexes of the type Cu$^I$P$_2$N$_2$.[8,16] However, heating this polymer in high boiling, coordinating solvents such as DMSO and DMF results in breaking of the weaker Cu–N bonds and release of [Cu(POP)]$^+$ into the solution leaving behind the imine-containing polymer backbone [Eq. (1)].

$$[\mathrm{Cu(N\hat{\ }N)(POP)}]^{+}{}_{n} \rightleftharpoons [(\mathrm{N\hat{\ }N})]_{n} + n\,[\mathrm{Cu(POP)}]^{+} \qquad (1)$$

Without the bulky phosphine groups and cationic charge of the copper, the polymers are inferred to aggregate into the fibrous structure of the gel matrix observed by scanning electron microscopy (SEM; Figure S19). In DMF, cooling of the solution appears to allow the [Cu(POP)]$^+$ groups to reattach to the vacant pyridyl imine sites, restoring the polymers and dissolving the gel. In DMSO, we infer that the lower solubility of the polymers results in phase separation due to greater aggregation, rendering the process irreversible. This mechanism is different than the one that we proposed to explain the heat-set gelation in a related system,[3c] in that we do not propose here that Cu$^I$ remains in the polymer.

In order to characterize the PL observed at high temperatures, the [Cu(POP)]$^+$ complex and metal-free polymer backbone [(N^N)] were isolated and their photoluminescence spectra were measured separately. Compound **3**, [Cu(POP)(CH$_3$CN)$_2$]BF$_4$, was synthesized according to a modified literature procedure (SI Section S1.4) and was found to show no luminescence. The demetallated polymer backbone was isolated by forming a gel (1.5 wt. % **1** in DMSO), then washing the gel repeatedly with DMSO until no [Cu(POP)]$^+$ was detected in the washings by NMR. The spectrum provides a good match with the PL of the gel formed in solution (Figure 1), from which we infer that the organic polymer backbone is responsible for the PL emission observed.

When polymer **1** was deposited as a thin film on Spectrosil, neither thermochromism nor PL shift was observed upon thermal annealing. Differential scanning calorimetry (DSC) measurements of the solid polymer showed no evidence of ligand rearrangement or other transitions taking place up to 250 °C. These results indicated that the transition observed in solution did not take place in the solid state due to heating. Cyclic voltammetry studies of polymer films, formed through drop casting **1** onto Pt electrodes, were undertaken. The voltammogram showed a peak at 1.2 V during the first cycle which was attributed to the oxidation of $Cu^{I}$–$Cu^{II}$ (SI Figure S20). This peak was diminished in subsequent cycles and the film changed color from red to yellow. This electrochromic behavior was attributed to the loss of the copper ions from the polymer backbone and indicates that an applied potential can bring about a transition similar to that observed in solution with a temperature change.

LEC devices fabricated with polymer **1** showed a similar color transition in electroluminescence as the PL transition observed in the solution phase. The LEC devices were fabricated by spin coating polymer **1** from DCM/DMF mixture onto PEDOT:PSS-coated ITO before thermally depositing an aluminum cathode on top. The polymer showed electroluminescence with an onset voltage of approximately 4 V and luminescence up to 3 $Cd\,m^{-2}$. The I-V-L spectrum for the device is shown in the SI Figure S21. At low voltage ($V_{app} < 6$ V) the devices emitted light in the IR region of the spectrum. However, as the voltage was increased, a blue shift in emission was observed, reaching a $\lambda_{max}$ of 580 nm at 20 V. The color shift upon increased voltage could clearly be seen in the photographs taken from the pixels in operation (inset in Figure 2 a).

The electroluminescence spectra of the devices operating at a low bias correspond well with the photoluminescence observed for the polymers in solution at low temperature (Figure 2 a). Notably, the electroluminescence spectra of the polymers at high bias correspond well with the PL spectra of the gel. This indicates that a similar transition may be taking place in the devices with the application of voltage as is observed in solution at high temperatures.

As described previously in the literature, the onset of light emission in this type of LEC device occurs after the formation of double layers at the electrode interfaces.[7a,11] Under the influence of the external bias, the $BF_4^-$ ions start to migrate toward the ITO electrode while positively charged polymer accumulates at the negative electrode. The electroluminescence spectrum that consists of mixed MLCT and ligand-centered π-π* transitions, blue shifts under strong bias (Figure 2). As the applied bias is increased, the $[Cu(POP)]^+$ ions become detached from the polymer and drift toward the cathode. The loss of nonluminescent $[Cu(POP)]^+$ complexes from the polymer backbone is inferred to result in a new higher energy emission peak comparable to the PL spectrum of the metal free N^N ligand (gel). Therefore we conclude that the ratio of the MLCT transition to the ligand-centered π-π* transition decreases as the metallopolymer loses its metallic character under strong bias (Figure 2 b). Therefore the final emission originates from the ligand-centered π-π* transitions and is in between the HOMO and the new LUMO states formed in the absence of copper.

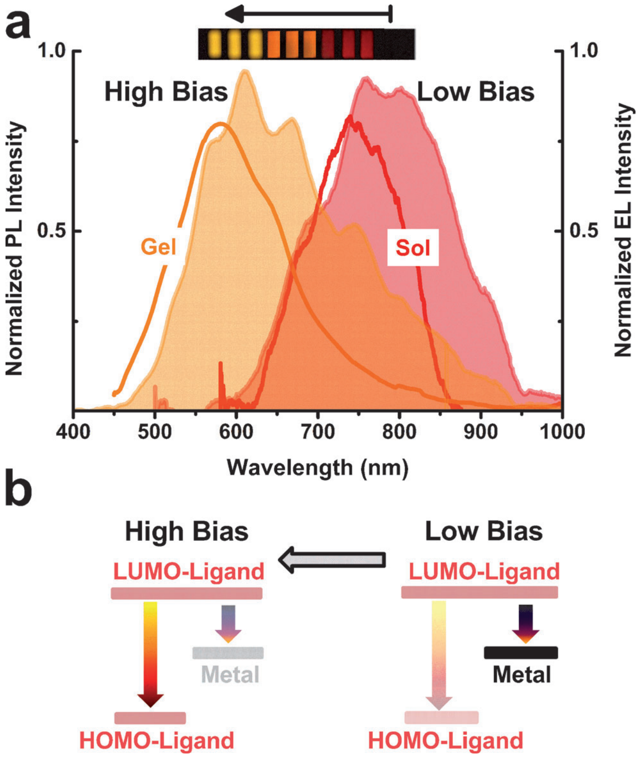

***Figure 2.*** a) Photoluminescence spectrum of the polymer solution in DMF (1 wt.%) (red), corresponding gel (orange), and electroluminescence spectrum of the device at low bias (shaded red) and high bias (shaded orange). Arrows indicate the corresponding axis for PL and EL. Inset: series of pictures taken of the pixel at increasing voltages. b) Schematic energy level diagram showing the dominant transition giving rise to electroluminescence emission for the device at low and high bias.

In order to understand the driving force behind the transformation in the solid state, experiments were undertaken to measure the effect of temperature on the device. Current densities of up to 1 $A\,cm^{-2}$ were reached at bias voltages above 4 V. This caused a temperature rise in the device, measured at 74 °C on the ITO side of the device and estimated to reach up to 86 °C inside the device based on heat transfer calculations (SI Section S6). DSC measurements of the bulk polymer indicate that no transitions take place up to this temperature. Moreover, devices which had been thermally annealed at 160 °C immediately before testing were found to behave identically to devices that had not been preheated and started emitting in the IR region when a low bias was applied.

Remarkably, the EL shift in the LEC devices appears to be quasi-reversible (Figure 3). The time required for recovery from yellow emission to IR depended on the device history. When the applied voltage stayed at moderate levels (< 8 V), pixels regained their red emission rapidly when the voltage was lowered. However, once the voltage was increased to

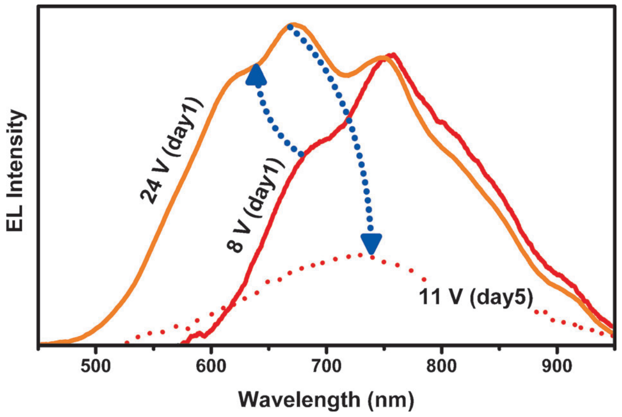

***Figure 3.*** EL spectra showing the emission of the ionic transition metal complex (iTMC) LEC devices at different voltages and over time. The initial bias was increased from 8 V (red) up to 24 V (orange) until the yellow emission was persistent. The dotted red line shows the EL spectrum taken after five days.

24 V, and the devices emitted yellow light, re-biasing the device to low voltages did not initially result in IR emission. However, when the devices were measured after five days, the emission band had shifted to longer wavelength and red emission was restored. This is thought to be due to the $[Cu(POP)]^+$ complexes re-coordinating to the vacant pyridylimine coordination sites, regenerating the metallopolymer, as we propose to explain reversible gel formation in DMF solution. Some irreversible reorganization of the polymer following the application of high bias is likely to account for the lower emission intensity observed after five days.

The technique of subcomponent self-assembly thus provides a facile approach to the synthesis of conjugated dynamic-covalent metallopolymers, which can be readily fabricated into functional LEC devices. The dynamic nature of the polymers allows them to reconfigure and to restore their structure resulting in changes in their rheological and photophysical properties. In solution this gives rise to thermochromic, heat-set gels and in the solid state to LEC devices that shift their electroluminescence in response to applied voltage. These readily observed transitions make the polymers suitable for a variety of sensing,[12] optoelectronic,[13] and molecular logic applications.[14] Investigations are currently underway to tune the photophysical and rheological properties of the polymers through the use of different amine and aldehyde subcomponents.

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