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Self-assembled zinc(II) Schiff base polymers for applications in polymer light-emitting devices†

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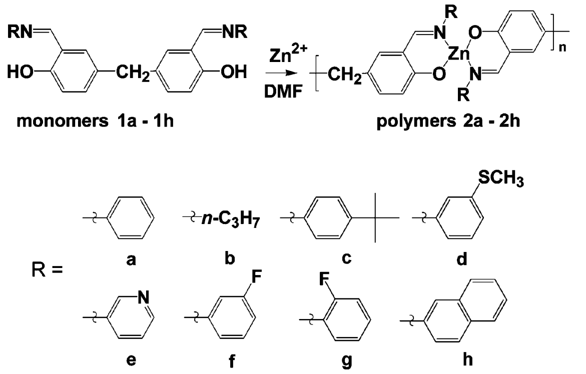
Thermally stable zinc(II) Schiff base polymers (decomposition temperature up to 461 °C; M_n = 13580 to 20440) formed by self-assembly reactions of zinc(II) salts and salicylaldimine monomers exhibit blue to yellow PL with quantum yields up to 0.34 in DMF; PLEDs employing these polymers as emitters give green or orange EL with turn-on voltage at 5 and 6 V and maximum efficiency of 2.0 and 2.6 cd A^{-1} respectively.

Transition metal complexes with Schiff base ligands are promising materials for optoelectronic applications due to their outstanding photo- and electroluminescent (PL and EL) properties, and the ease of synthesis that readily allows structural modification for optimization of material properties.[1–5] Hamada and coworkers pioneered Zn(II) Schiff base complexes as blue to greenish-white emitters for EL devices.[3] Che *et al.* have recently demonstrated Pt(II) Schiff base triplet emitters as yellow dopants for organic light-emitting devices (OLEDs) and achieved white EL with those complexes.[5]

Polymers are widely regarded as promising materials for optoelectronic devices. Polymer light-emitting devices (PLEDs) generally give superior performance including lower turn-on voltage, ease of preparation in terms of large-area displays and greater stability with no recrystallization problem as that encountered for small molecules in OLEDs.[6–9] Studies on polymers having metal-Schiff base as building blocks for PLED applications, however, remain sparse, probably due to the complication involved in polymer preparation. Tao *et al.* reported a Zn Schiff base polyurethane emitter for EL devices; nonetheless, the estimated quantum efficiency is only 0.005%.[10] We envision that the recent development of self-assembled metal coordination polymers[11–14] can be extended to the synthesis of metal Schiff base polymers with well-defined architectures and interesting photophysical properties. In this work, we demonstrate a family of self-assembled Zn(II) Schiff base polymers (**2a–2h**) that are thermally stable, structurally diverse and easily synthesized; they also possess tunable EL emissions for PLEDs (Scheme 1).

The number-average molecular weight (M_n) of the polymers ranges from 13580 to 20440, as determined using Gel Permeation Chromatography (GPC) with polystyrene as a standard in THF (tetrahydrofuran) at 35 °C. The monomers, which are soluble in THF and $CHCl_3$, can be synthesized in up to 80% yield by condensation of salicylaldehyde with either alkylamines or arylamines in CH_3OH.

Fig. 1 depicts the ^1H NMR titration studies on the formation of **2a** on the left and that of the model compound, bis(*N*-phenylsalicylaldiminato)zinc(II), on the right. The spectra were recorded in DMSO-d_6 by varying the molar ratio of ligand *N*-phenylsalicylaldimine or monomer **1a** to $Zn(OAc)_2{\cdot}2H_2O$. At ligand : Zn^{2+} of 2 : 1 for the model compound, the free ligand NMR signals at 7.0 or 9.0 ppm were not observed; the signals at *ca.* 6.5 to 8.5 ppm correspond to the aromatic protons of *N*-phenyl and benzene rings of the coordinated salicylaldiminato unit. Increasing the ligand : Zn^{2+} ratio to 2 : 3 does not change the spectrum; this implies that the bis(salicylaldiminato) zinc complex is stable and its formation is stoichiometric. At the **1a** : Zn^{2+} ratio of 1 : 1, the broad peaks at *ca.* 6.5, 7.0–7.5 and 8.5 ppm resemble the corresponding aromatic proton signals of the model compound for ligand : Zn^{2+} of 2 : 1; the free monomer signals were again not detected. These results reveal facile formation of the stable polymer bearing bis(salicylaldiminato) zinc(II) moieties as depicted in Scheme 1.



Scheme 1 Synthesis of Zn Schiff base polymers **2a–2h**.

Thermal gravimetric analysis (TGA) showed that the decomposition temperature (T_d) of the polymers range from 389 (**2g**) to 461 °C (**2h**) under nitrogen atmosphere.† No phase transition was observed in differential scanning calorimetry (DSC) up to 300 °C, indicating that glass transition temperature (T_g) of the polymers are high. Enhancement of thermal stability introduced by polymerization (T_g of the model compound is only 170 °C) offers a valuable property for PLED applications.

To further study the potential of these polymers in application of PLEDs, surface morphology of the films was studied using atomic force microscopy (AFM). Fig. 2 shows the topographic image of **2c** under characterization. The thin film (40 nm) has surface roughness of 0.8 to 1.5 nm in the 5 × 5 μm^2 scan area. The morphological smoothness reveals that only a limited number of pin holes would be introduced into the device layers with this polymer. The film is of

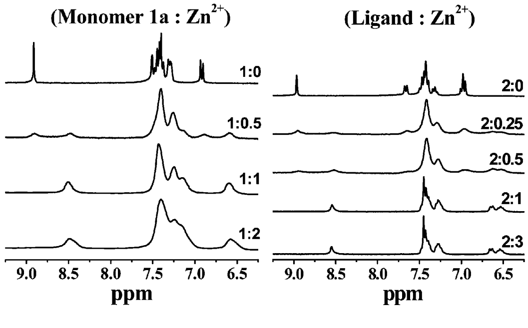


Fig. 1 ^1H NMR titration spectra of **2a** and the model compound, bis(*N*-phenylsalicylaldiminato)zinc(II).

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† Electronic supplementary information (ESI) available: synthetic procedures and physical data of the polymers and monomers as well as fabrication procedures for the PLEDs. See http://www.rsc.org/suppdata/cc/b4/b412762e/

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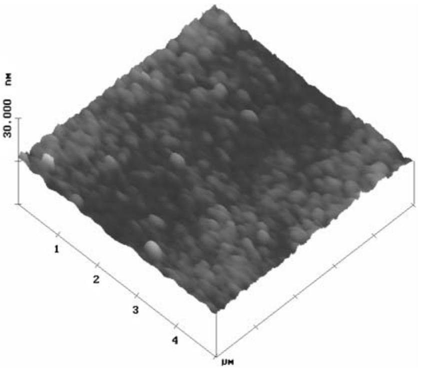

Fig. 2 AFM (topographic) image of a 40 nm film of **2c** on ITO glass.

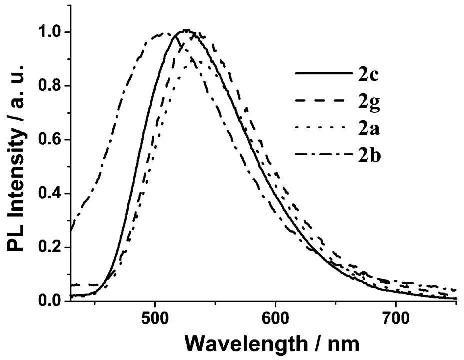

Fig. 3 PL spectra for the films of **2a**, **2b**, **2c** and **2g**.

optical quality and provides a good contact with the next layer of deposited material.

Polymers **2a–2h** exhibit similar absorption features in DMF (*N*,*N*-dimethylformamide) solution, with λ_{max} at 280–309, 311–358 and 408–427 nm. For example, **2c** shows strong absorption bands at 291 and 311 nm (a_{max} = 24.3 × 10^4 and 26.5 × 10^4 g^{-1} dm^3 cm^{-1} accordingly), assigned to ligand-centered (LC) π–π* transitions of the *p*-phenyl ring and salicylaldimine ligand, in addition to a shoulder at 413 nm.

PL emission assigned to intra-ligand ^{1}(π*–π) fluorescence and spans from blue to yellow are obtained for the polymers in DMF solution (blue for **2b**, green for **2a** and **2c**, and yellow for **2h** with λ_{max} at 458, 508, 501, and 562 nm respectively on excitation at 360 nm). The quantum yields (*Φ*) range from 2% for **2e** and **2h** to 34% for **2f**. The emission colour can be fine-tuned easily upon incorporation of different functional groups, R, along the polymer chains (Scheme 1). On the other hand, the films of most of these polymers emit in yellowish orange with PL λ_{max} at 534–538 nm, except for **2b** where λ_{max} is at 509 nm and for **2c** with λ_{max} at 526 nm (Fig. 3). The emission from the film of **2g** (λ_{max} 534 nm) shows a Stokes shift of approximately 870 cm^{-1}, attributed to excimer formation resulting from π–π aromatic stacking interaction in the solid state. Polymer **2c** exhibits a more greenish emission compared to the other polymers, probably due to the presence of the bulky *tert*-butyl groups which retards aggregation of the polymer chains and suppresses excimer formation.

Polymers **2c** and **2g** were fabricated into PLEDs **A** and **B** using standard spin-coating and vacuum deposition methods.† The configuration is ITO (indium–tin–oxide)/PEDOT : PSS (3,4-polyethylenedioxythiophene : polystyrenesulfonate, 30 nm)/polymer (30–50 nm)BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 20 nm)/Alq$_3$ (tris(8-quinolinonato)aluminium, 20 nm)/LiF (0.5 nm)/Al (200 nm). Device **A** (with **2c**) at a bias voltage of 8 V shows a green emission with λ_{max} at 536 nm and CIE_1931 coordinates of x = 0.30 and y = 0.55; the EL intensity is augmented with increasing bias voltage. The turn-on voltage is approximately 5 V, the maximum efficiency of the device is 2.0 cd A^{-1} at 8 V and the maximum luminance of 3120 cd m^{-2} was obtained at 15 V. Device **B** (with **2g**) exhibits an orange EL (λ_{max} at 584 nm, CIE_1931 coordinates: x = 0.54, y = 0.45) with the onset voltage at 6 V. The maximum efficiency and luminance are 2.6 cd A^{-1} at 8 V and 2460 cd m^{-2} at 15 V respectively. Neither of the EL from devices **A** and **B** resembles their corresponding PL from thin films (Fig. 3 and inset of Fig. 4). This is presumably due to the EL and PL emissions originating from different excited states and/or ground states. The EL spectra obtained at lower energy could be due to recombination of excitons at the narrow interface of the films in PLEDs, while the broad PL spectra could originate from the bulk polymer film upon UV excitation.[15]

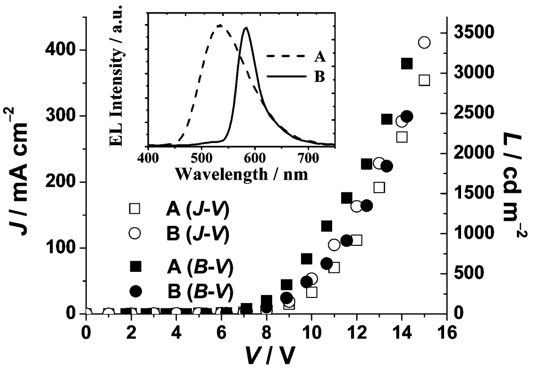

Fig. 4 Voltage–current density–luminance (*V-J-L*) curves and EL spectra of devices **A** (**2c**) and **B** (**2g**).

In summary, we have developed a family of Zn(II) Schiff base polymers based on self-assembly reactions. These polymers, which exhibit different emission energies in solvent and as thin films, possess good thermal stability, processing abilities and are easy to prepare. They provide a new entry to the development of polymeric materials for PLEDs.

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