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Design, synthesis, characterization, and fluorescent studies of the first zinc-quinolate polymer†

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We report the design, synthesis, and characterization of the first Znq$_2$-copolymers, which demonstrate excellent photoluminescence properties, with emission wavelengths ranging from the blue to the yellow, while retaining full solution processability.

The design and characterization of faster and brighter electroluminescent devices has focused in recent years on either small organic compounds or conducting polymers.[1–3] In particular, metalloquinolates, such as aluminium tris(8-hydroxyquinoline) (Alq$_3$), have attracted significant attention due to their excellent solid-state properties including good electron mobility and high luminescence.[4] Recent reports have suggested that the zinc analog of Alq$_3$, zinc bis(8-hydroxyquinoline) (Znq$_2$) has a better injection efficiency, a lower operating voltage, and higher quantum yields than the widely used Alq$_3$.[5] However, as in the case with Alq$_3$, the major drawback of Znq$_2$ is the need for vacuum deposition for thin film formation. We recently reported a polymer-supported Alq$_3$ system that is able to overcome this processable limitation.[6] Herein, we described the next generation of fluorescent material by combining our polymerization strategy with the outstanding photoluminescence and electroluminescence properties of Znq$_2$ in the preparation and characterization of the first Znq$_2$-functionalized polymers.

The non-metallated monomer synthesis has been reported before and is based on norbornene, which can be polymerized using ring-opening metathesis polymerization (ROMP).[7] An alkyl chain, which links the hydroxyquinoline to the norbornene unit, was introduced to decouple the motion of the polymer backbone from the metalloquinolate complex and to increase solubility.

Monomer functionalization can be carried out as shown in Fig. 1. One equivalent of monomer **1** was added to one equivalent of diethylzinc, ensuring complete metallation without the addition of two monomers to one zinc atom as determined by elemental analysis, followed by a second equivalent of 8-hydroxyquinoline, resulting in the formation of the zinc-monomer **2** in quantitative yields. To tune the optical properties of the resulting polymer, we substituted 8-hydroxyquinoline with a variety of functionalized quinolines; the structures and abbreviations are shown in Fig. 1. Polymerization of **2** was carried out using the initiator **3** in chloroform at room temperature and was complete after 12 hours.[7] To tailor the solubility of our polymeric material, monomer **2** was co-polymerized with a spacer monomer, nonylnorbornene **4**, in ratios of 1 : 1, 1 : 5, 1 : 10, and 1 : 20 (**2**/**4**), resulting in copolymers that were readily soluble in halogenated solvents. For the optical properties characterization of the copolymers, the 1 : 20 ratios were used unless otherwise noted.

All copolymers were characterized using NMR, UV/vis, and fluorescence spectroscopy, with the results being summarized in Table 1. The molecular weights of the copolymers ranged from 8,000 to 40,000, with polydispersities between 1.5 and 2.5 as determined by GPC. The UV/vis and fluorescence spectra were recorded in dry chloroform. Fig. 2 shows the solution fluorescence spectra of all copolymers, excited at 380 nm, except for the **Naph** copolymer which was excited at 330 nm.[8] As illustrated in Fig. 2, the emission can be tuned in solution from blue (427 nm) to yellow (565 nm) through variations of the second functionalized quinoline. These results clearly demonstrate that the fluorescence properties of the material can be tuned in solution and that the polymer

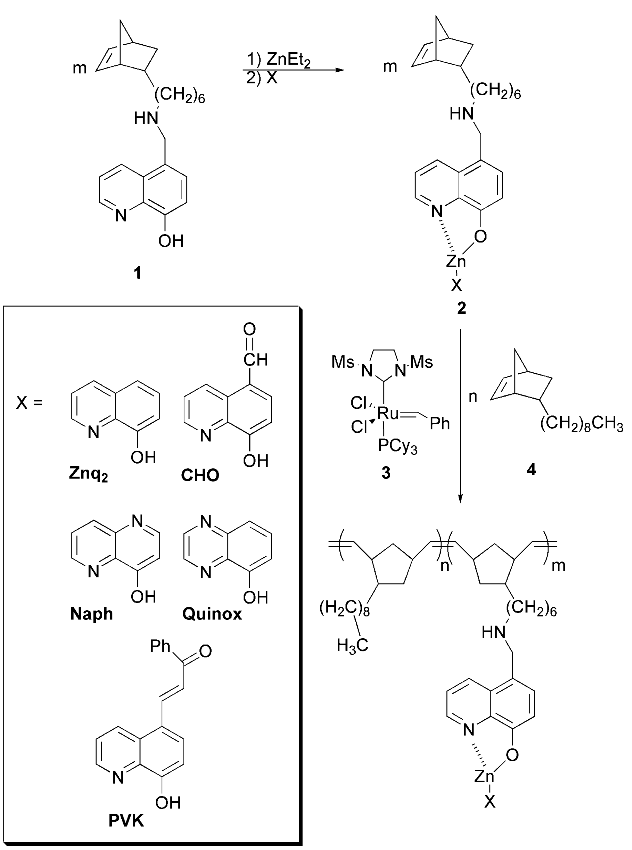

Fig. 1 Synthesis and polymerization of zinc-monomers.

Table 1 Photoluminescence data for Znq$_2$-copolymers.

Name	Absorption λ_{max}	Solution emission λ_{max}	Solid-state emission λ_{max}	Relative quantum yields
Alq$_3$	381	525	519^a	1.0
Znq$_2$	379	542	542^a	1.3
1 : 1 Znq$_2$	378	544	548	1.8
1 : 5 Znq$_2$	374	543	520	3.9
1 : 10 Znq$_2$	375	545	512	2.0
1 : 20 Znq$_2$	378	546	505	0.30
CHO	381	503	487	2.2
PVK	373	565	545	0.33
Naph	325	427	445	0.37
Quinox	379	510	467	0.44

^{a} Reported in T. A. Hopkins, K. Meerholz, S. Shaheen, M. L. Anderson, A. Schmidt, B. Kippelen, A. B. Padias, J. H. K. Hall, N. Peyghambarian and N. R. Armstrong, *Chem. Mater.*, 1996, **8**, 344–351.

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† Electronic supplementary information (ESI) available: experimental information on prepared compounds and characterization. See http://www.rsc.org/suppdata/cc/b4/b402289k/

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backbone does not interfere with the optical properties of the Znq_2 moiety.

The relative quantum yields were calculated based on Alq_3 as the standard and are summarized in Table 1. As suggested by other reports, Znq_2 has a higher quantum yield than Alq_3.[5] Interestingly, our 1 : 1, 1 : 5, and 1 : 10 Znq_2-copolymers have even higher quantum yields than their small molecule counterpart. It is not until the concentration of the Znq_2-monomer drops below 10 mol% of the total copolymer composition that the quantum yields decrease below that of pure Znq_2. The increase in quantum yields going from Znq_2 to the 1 : 1 Znq_2-copolymer to the 1 : 5 Znq_2-copolymer indicates the possibility of some self-quenching occurring at higher Znq_2 concentrations. It is noteworthy that all 1 : 20 copolymers have approximately the same quantum yields, except for the **CHO**-copolymer, which is significantly higher than that of Znq_2 suggesting an exceptional material for electroluminescence.

Essential for the use of these materials are their solid-state properties. To characterize the solid-state properties of all copolymers, thin films were spun on quartz slides, with thicknesses ranging between 200–400 nm as determined by ellipsometry. The fluorescence spectra were recorded at an excitation wavelength of 380 nm (**Naph** at 330 nm) and are shown in Fig. 3, with the λ_{max} reported in Table 1. Similar to the solution studies, the emission colors of the films range from the blue to the yellow. We also investigated the influence of the lumophore density on the solid-state properties. The 1 : 1 copolymer emission is red-shifted in comparison to the emission of the 1 : 20 copolymer. This phenomenon has previously been described in relation to Alq_3, where the emission wavelength is dependent on the packing of the quinolate ligands. The shorter the interligand contacts, the more red-shifted the emission.[9] Regardless of the lumophore concentration and the quinoline ligand used, the emission of the thin films again indicate that the polymer backbone does not inhibit fluorescence, even in the solid-state. Preliminary experiments into the conductivity of the films were measured using a four-point probe and resulted in conductivities ranging from 12 S cm^{-1} for the 1 : 1 Znq_2-copolymer to 3.6 S cm^{-1} for the 1 : 20 Znq_2-copolymers. This suggests that our polymers are able to support a current, another prerequisite for their use in electroluminescent devices.

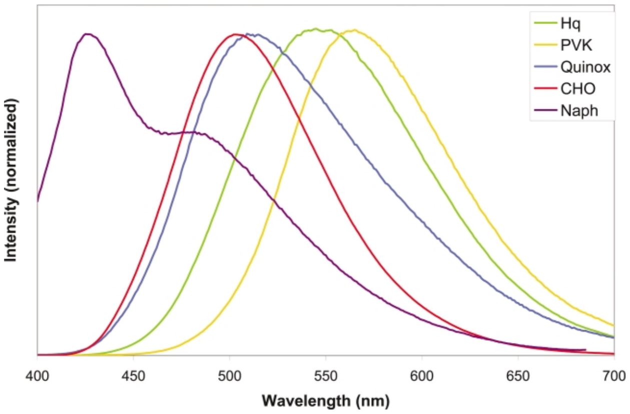

Fig. 2 Solution emission of Znq_2-copolymers.

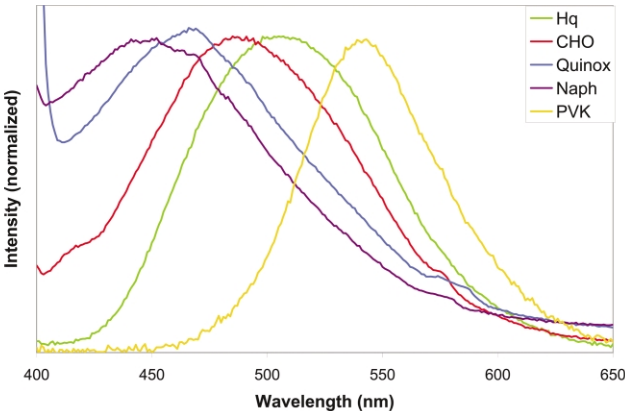

Fig. 3 Solid-state emission of Znq_2-copolymers.

In conclusion, we have synthesized and characterized the first Znq_2-based monomers and copolymerized them with a spacer monomer *via* ROMP. The resulting copolymers retained the photoluminescent properties of the metalloquinolates while gaining the added advantage of being solution processable. Our copolymers demonstrated extremely high quantum yields in solution, far exceeding that of the extensively used Alq_3. Furthermore, the emission color of the polymers could be tuned through simple ligand functionalization. This study suggests that the Znq_2-copolymers are excellent candidates for use in organic electroluminescent devices and efforts towards the realization of this goal are currently being carried out.

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8 The nomenclature of the polymers is as follows: **X**-polymer, where **X** is equal to the functionality on the modified 8-hydroxyquinoline ligand, as shown in Fig. 1. **Naph** was excited at a different wavelength than the other polymers due to the strong absorption in the UV/Vis at 330 nm, which was not seen for the other polymers.

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