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Design and Synthesis of Alq$_3$-Functionalized Polymers

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Aluminum tris(8-hydroxyquinoline) (Alq$_3$) is one of the most stable and fluorescent solid-state materials, making it the emission and electron-transport layer of choice in organic light-emitting diodes (OLEDs).[1−5] One limitation associated with Alq$_3$ is its poor processability. The current trend in the fabrication of OLEDs is solution-processing; however, Alq$_3$ must be vacuum-deposited.[6,7] One possible solution to this problem is the use of polymers containing Alq$_3$ pendant groups. These polymers could combine the fluorescent properties of Alq$_3$ while maintaining the processability of a polymer, allowing for the low-cost manufacturing techniques such as solution-processing and possibly ink-jet printing.[6] Herein, we report the design and synthesis of such a polymer-supported Alq$_3$.

Alq$_3$ is a thermally stable, highly fluorescent material with excellent electron-transport mobilities.[7,8] Its usual blue-green luminescence can be either blue- or red-shifted through (a) the addition of substituents or (b) the introduction of optically inactive spacer molecules into the crystalline network of Alq$_3$.[5,7−9] While most research activities have been focused on manipulating the optical properties, the problem with the processability of Alq$_3$ has not been solved. One possible solution that has been utilized to enhance processability is the introduction of Alq$_3$-doped polymers, where the Alq$_3$ complex is embedded within a polymer matrix.[10,11] However, phase separation can occur, leading to poor optical properties in these systems.[12] To circumvent the phase separation problems, Alq$_3$ can be covalently attached to the polymer backbone. However, the only reported Alq$_3$-functionalized polymer to date is a condensation polymer that was functionalized with Alq$_3$ in a postpolymerization step.[12] As a result of this postpolymerization step, the probability of having a fully functionalized polymer without cross-linking is a major concern. In contrast, our design strategy is based on a fully functionalized monomer that can be polymerized in a controlled fashion, thereby eliminating any cross-linking. Additionally, we are able to control and alter the polymer structure by using comonomers to tune the polymeric properties.

Our monomer design requires two structural motifs: (1) a polymerizable unit that allows for a high degree of control during the polymerization and (2) an alkyl spacer between the polymerizable unit and the Alq$_3$ to decouple the backbone from the Alq$_3$ group. Norbornene was chosen as the polymerizable unit. It can be polymerized using ring-opening metathesis polymerization (ROMP), a method that has a high tolerance to many functional groups.[13−16] Furthermore, ROMP is often a living polymerization method resulting in polymers with controlled molecular weights and low polydispersities and also allows for the formation of block copolymers.[14,17,18]

The synthesis of the monomer (Scheme 1) began with the functionalization of the norbornene **1**, formed using a Diels−Alder reaction between allyl bromide and cyclopentadiene. Attachment of a bromoalkyl chain using Grignard chemistry followed by the conversion of the bromide to the nitrile and subsequent reduction of the nitrile resulted in the precursor **4** in an overall yield of 51%. Compound **4** was then coupled to **6**,[19] followed by the reduction of the resulting imine to yield monomer **8**.

The formation of the Alq$_3$-functionalized monomer **9** was achieved by adding monomer **8** to 10 equiv of triethylaluminum followed by 20 equiv of 8-hydroxyquinoline (Scheme 2). This resulted in the formation of 1 equiv of **9** and 9 equiv of nonfunctionalized Alq$_3$. This procedure was developed to ensure full metalation of each monomer without coordination of two monomer units onto the same aluminum center, thereby preventing any cross-linking during the polymerization.[20] The 9:1 mixture (Alq$_3$:**9**) was used directly in the polymerizations, which were carried out in chloroform at room temperature using the ruthenium catalyst **11**. A 50:1 monomer-to-catalyst ratio was fully polymerized within 12 h. After complete polymerization, the excess Alq$_3$ was removed from the polymer through extensive washings with methanol and methylene chloride, yielding a polymer without any impurities. Solubility of the polymer proved to be limited. However, solubility could be increased by copolymerizing **9** with 5-nonylnorbornene **10**, a nonfunctionalized monomer, which was synthesized in a similar manner as **2**. The optimal ratio of functional monomer to spacer monomer (**9**:**10**) (i.e., the highest percentage of **9** while retaining full and controlled solubility) was investigated through the synthesis of a series of copolymers (Table 1). All copolymers with a **9**:**10** ratio of at least 1:4 could be fully solubilized in a 0.1% (v/v) chloroform/trifluoroacetic acid mixture. All resolubilized copolymers were characterized using gel permeation chromatography and showed polydispersities between 1.5 and 1.8. Differential scanning calorimetry did not show a glass-transition temperature or a melting temperature, while thermogravimetric analysis showed the onset of polymer decomposition at 250 °C.

Essential for the success of our polymer-supported Alq$_3$ strategy is that the copolymers retain the optical properties of Alq$_3$ and show no interference of the polymer coil with the emission properties. Therefore, we investigated the photoluminescence of the copolymers and monomer **8** and compared them to Alq$_3$.[21] The UV/vis absorption spectrum of monomer **8** shows a $\lambda_{\max}$ at 319 nm, corresponding to the low-energy singlet transition of the hydroxyquinoline group.[22] The absorption spectrum of Alq$_3$ as described in the literature and determined by us shows peaks at 372 and 316 nm.[23] The absorption spectra of all copolymers show identical peaks as that of Alq$_3$, indicating the same transitions taking place in our copolymer system as the ones known for Alq$_3$. The emission spectra of Alq$_3$ and the copoly-

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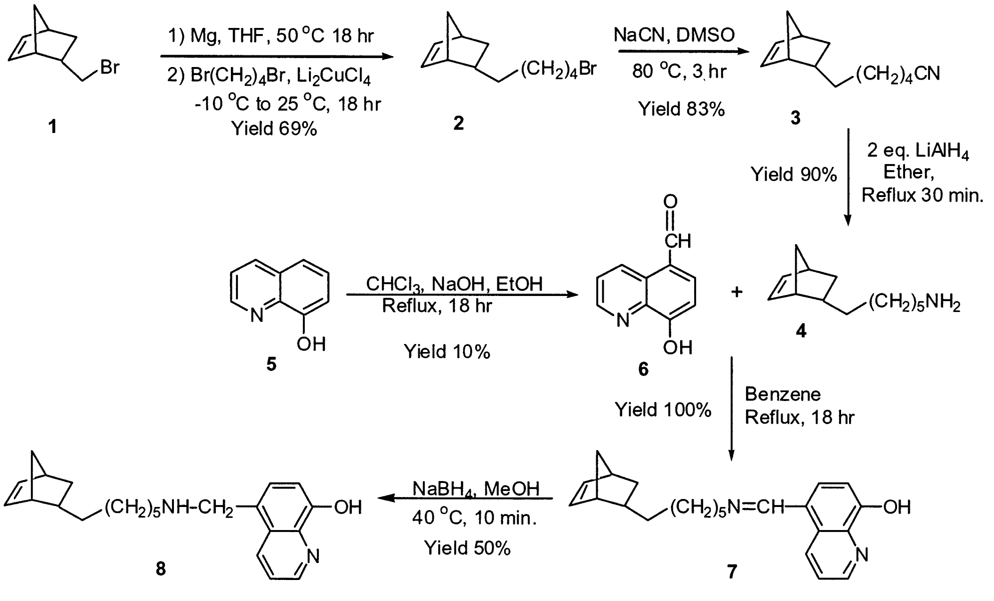
Scheme 1. Monomer Synthesis.



Scheme 2. Alq$_3$ Monomer Formation and Polymerization

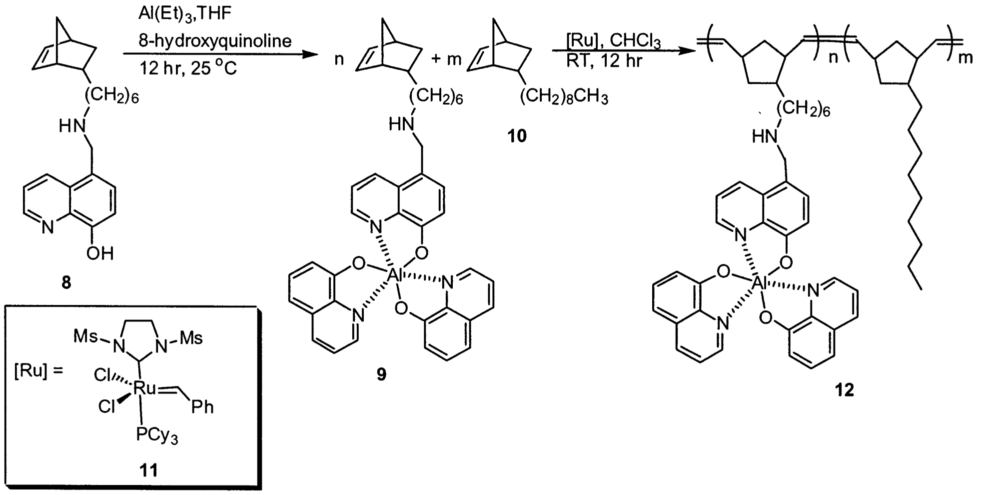


Table 1. Photoluminescence Data for 8, Alq$_3$, and a Series of Copolymers and Copolymer Characterization Data

sample	UV/vis concn (mg/mL)	UV/vis λ_{max} (nm)	fluores concn (mg/mL)	fluores λ_{max} (nm) [intensity]	M_n	M_w	PDI
monomer **8**	0.02	319					
Alq$_3$	0.1	316, 372	0.09	509			
1:4 (**9**:**10**) polymer	0.5	313, 370	0.05	512 [2633836]	68 000	104 000	1.53
1:5 (**9**:**10**) polymer	0.5	313, 371	0.05	509 [2364129]	55 000	94 000	1.71
1:10 (**9**:**10**) polymer	0.5	313, 373	0.05	506 [1727476]	57 000	100 000	1.74

mers were collected from 400 to 700 nm with an excitation wavelength of 380 nm. As shown in Figure 1, all copolymers fluoresce at the same wavelength as Alq$_3$ in solution, demonstrating that the emission properties of Alq$_3$ are retained. As expected, the ratio of Alq$_3$ monomer to the nonfunctionalized monomer did affect the intensity of the emission. The intensity shows a linear relationship with the percentage of Alq$_3$ present in the copolymer, as indicated by the data provided in Table 1. These studies clearly show that the optical properties of Alq$_3$ are preserved in the polymer and not affected by the polymer coil while in solution. Preliminary experiments of spin-casted copolymer solutions resulted in thin films that show fluorescence emission similar to that of Alq$_3$ in the solid state. An in-depth study of the solid-state behavior of the copolymers is currently underway.

In conclusion, we have demonstrated the first successful synthesis of an Alq$_3$-containing monomer and its chain-growth polymerization via ROMP. The polymerization was complete within 12 h under mild polymerization conditions. Solubility could be tailored via the incorporation of a comonomer. Most importantly, all copolymers retained the absorption and emission properties of that of Alq$_3$ in solution, indicating that the polymer coil does not interfere with the luminescence properties of the pendant Alq$_3$ groups. Preliminary experiments show that optical properties of our polymers in the solid-state are similar to the presented solution-state data. Future work will include studying

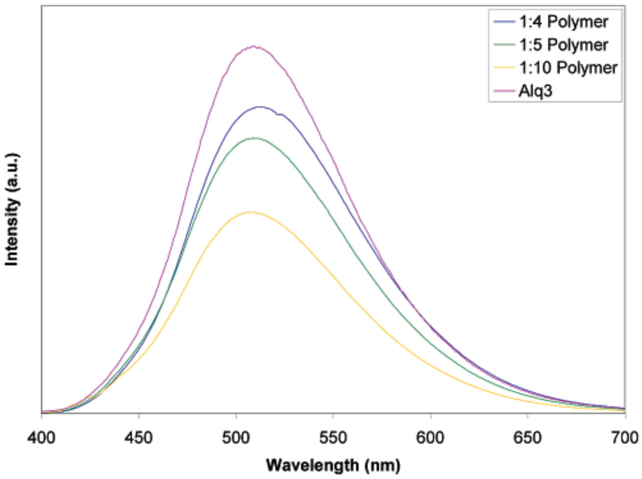


Figure 1. Emission spectra in $CHCl_3$ excited at 380 nm.

in-depth the solid-state properties of the polymers and the fabrication of OLEDs.

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Supporting Information Available: All experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−915.
(2) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610−3616.
(3) O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442−444.
(4) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815−817.
(5) Jang, H.; Do, L.-M.; Kim, Y.; Zyung, T.; Do, Y. *Synth. Met.* **2001**, *121*, 1667−1668.
(6) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121−128.
(7) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161−174.
(8) Hopkins, T. A.; Meerholz, K.; Shaheen, S.; Anderson, M. L.; Schmidt, A.; Kippelen, B.; Padias, A. B.; Hall, Jr., H. K.; Peyghambarian, N.; Armstrong, N. R. *Chem. Mater.* **1996**, *8*, 344−351.
(9) Brinkmann, M.; Gadret, G.; Muccini, M.; Taliani, C.; Masciocchi, N.; Sironi, A. *J. Am. Chem. Soc.* **2000**, *122*, 5147−5157.
(10) Affinito, J. D.; Martin, P. M.; Graff, G. L.; Burrows, P. E.; Gross, M. E.; Sapochak, L. Method of making molecularly doped composite polymer materials. U.S. Patent 6,228436, 2002.
(11) Antoniadis, H.; Roitman, D.; Miller, J. Organic electroluminescent device. U.S. Patent 5,719467, 1998.
(12) Lu, J.; Hlil, A. R.; Meng, Y.; Hay, A. S.; Tao, Y.; D'iorio, M.; Maindron, T.; Dodelet, J.-P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2887−2892.
(13) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043.
(14) Piotti, M. E. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 539−547.
(15) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.
(16) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749−750.
(17) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1996.
(18) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: New York, 1997.
(19) Clemo, G. R.; Howe, R. *J. Chem. Soc.* **1955**, 3552−3553.
(20) The statistical probability of having two monomer units attached to the same aluminum center is 0.1%. While this number is negligible and we do not observe any cross-linking, we are not able to exclude a limited amount of cross-linking at this point.
(21) Commercial Alq_3 was treated with the same chloroform/trifluoroacetic acid mixture as the copolymers. No changes in the optical properties before and after this treatment were detected.
(22) Ravi Kishore, V. V. N.; Aziz, A.; Narasimhan, K. L.; Periasamy, N.; Meenakshi, P. S.; Wategaonkar, S. *Synth. Met.* **2002**, *126*, 199−205.
(23) Halls, M. D.; Schlegel, H. B. *Chem. Mater.* **2001**, *13*, 2632−2640.
(24) Giraudi, G.; Baggiani, C.; Giovannoli, C.; Marletto, C.; Vanni, A. *Anal. Chim. Acta* **1999**, *378*, 225−233.
(25) Stubbs, L. P.; Weck, M. *Chem. Eur. J.*, in press.

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