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Poly(styrene)-Supported Alq_3 and BPh_2q

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ABSTRACT: We describe the synthesis of 8-hydroxyquinoline-tethered poly(styrene)s as modular precursors for functionalization with metalloquinolates to form either tris(8-hydroxyquinoline)aluminum (Alq_3) or 8-hydroxyquinoline biphenylboron (BPh_2q) pendant polymers. All polymers, both in solution and in the solid state, show similar luminescent properties as their corresponding reference compounds Alq_3 and BPh_2q while retaining excellent solution-processing properties. These results clearly indicate that the poly(styrene) backbone does not interfere with the photophysical properties of the pendant Alq_3 and BPh_2q chromophores but endows solution processability to the materials.

Introduction

The past decade has seen a considerable increase in the development of polymers functionalized with electroluminescent chromophores for applications as emission and electron-transport layers in organic light-emitting diodes (OLEDs).[1−7] These materials are of particular interest to industry because they allow for the use of low-cost solution-processing techniques, such as spin-coating or ink-jet printing in the fabrication of OLEDs. Among the most important and widely used chromophores in OLEDs is aluminum tris(8-hydroxyquinoline) (Alq_3). Alq_3 has excellent solid-state luminescent properties with reasonable electron-transport mobilities that are several magnitudes higher than its hole mobilities. Furthermore, it is known to form a thermally stable thin film, an important prerequisite for its use in electrooptical devices.[8,9] Recently, we have reported the first synthesis of an Alq_3 side-chain-functionalized polymer by employing tethered norbornenes as monomers and using ring-opening metathesis polymerization (ROMP) as the polymerization method of choice.[2] Furthermore, we have shown that the resulting polymers exhibit outstanding emission properties in solution and thin films. While these studies clearly demonstrated the concept of Alq_3 tethered polymers, ROMP-based polymers are limited to highly strained monomers such as norbornene or cyclooctene that are expensive, thereby limiting the potential use of these polymers in everyday applications. Therefore, the need for a commodity polymer as polymeric scaffold for Alq_3 is evident. Within the past 12 months, polymers containing Alq_3 that are based on PMMA derivatives have been reported.[3] Herein, we report the functionalization of well-defined poly(styrene)s with 8-hydroxyquinoline side chains. Poly(styrene) is widely used as polymeric scaffold because it offers considerable synthetic flexibility with regard to polymer derivatizations.[4] Furthermore, from a photochemistry viewpoint, poly(styrene) is relatively inert toward electron or energy transfer because of its very high oxidation and low reduction potentials with no low-lying excited states. Finally, poly(styrene) is inexpensive, is readily soluble in common solvents, and shows good thermal stability and film formability. Therefore, poly(styrene) is the polymer scaffold of choice for metalated 8-hydroxyquinoline complexes. Another important characteristic of our poly(styrene)-supported 8-hydroxyquinoline system is that it is modular in regard of the metal functionalization step; i.e., any metal that is able to coordinate to 8-hydroxyquinoline can be employed. Quinoline-based complexes of metals such as zinc[5] or boron[6] have been used extensively in the literature as potential OLED materials. However, reports on polymer supported analogues of such complexes are rare. The only report on polymer-supported boron−quinolate complexes is from the Jäkle group. In 2004, Jäkle and coworkers described the synthesis of BR_2q-based poly(styrene)s as potential materials for OLEDs.[7] In their system, the formation of the boron−quinolate complexes is based on the highly selective reaction of an 8-hydroxyquinoline with a poly(4-disubstituted thienyl−borylstyrene) precursors occurring at the thionyl−boron bond rather than a phenyl−boron bond. In contrast to the Jäkle system, our research design is based on a polymer-supported quinoline as a ligand for boron complexation and not a boryl styrene. Therefore, our 8-hydroxyquinoline-functionalized polymers can be viewed as modular backbones for the design of polymer-based metalloquinolates through the complexation of a variety of metals followed by the addition of free hydroxyquinoline ligands.

Results and Discussion

Synthesis. The synthetic route toward 8-hydroxyquinoline-functionalized poly(styrene)s is outlined in Scheme 1. The synthesis commences with the copolymerization of styrene and *p*-(chloromethyl)styrene via free radical polymerization. Ratios of 2:1 and 9:1 of styrene and *p*-(chloromethyl)styrene were copolymerized as outlined in the literature using AIBN as the initiator, yielding the copolymers P33Cl ($M_n = 6100$, PDI = 1.90) and P10Cl ($M_n = 6400$, PDI = 1.50), respectively.[10] The chemical compositions of both copolymers were characterized by ^1H NMR and elemental analyses. Elemental analysis data of P33Cl [calculated based on the repeating unit $(C_{25}H_{25}Cl)_n$: C, 83.20%; H, 6.98%; Cl, 9.82%. Found: C, 82.47%; H, 7.01%; Cl, 10.09%] and P10Cl [calculated based on the repeating unit $(C_{81}H_{81}Cl)_n$: C, 89.26%; H, 7.49%; Cl, 3.25%. Found: C, 88.66%; H, 7.45%; Cl, 3.47%] clearly demonstrate that the copolymers have the same monomer composition as the

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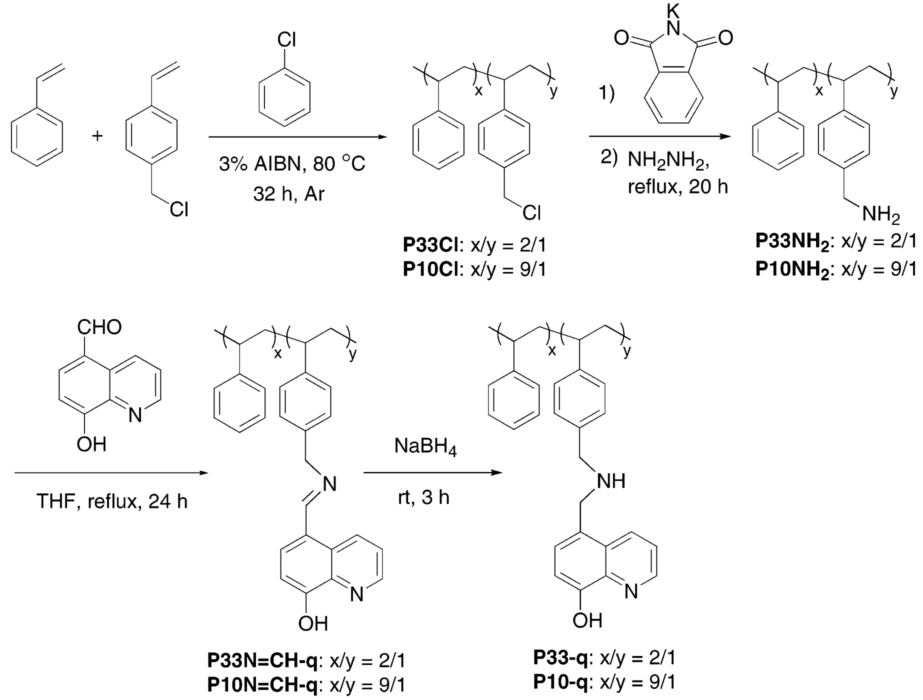
Scheme 1. Synthesis of 8-Hydroxyquinoline-Functionalized Poly(styrene)s



monomer feed. The conversions of the chloromethylated poly(styrene)s to their corresponding amine derivatives were carried out according to literature procedures,[10] by first treating the copolymers with potassium phthalimide in DMF to yield the phthalimide-derivatized polymers quantitatively, followed by the reaction with hydrazine monohydrate in ethanol to provide the fully amino-functionalized polymers P33NH$_2$ and P10NH$_2$. Coupling of 5-aldehyde-8-hydroxyquinoline with P33NH$_2$ or P10NH$_2$ afforded the corresponding Schiff bases P33N=CH-q and P10N=CH-q that were reduced to the corresponding amines with NaBH$_4$ to yield the desired 8-hydroxyquinoline-functionaliezd polymers P33-q and P10-q. Figure 1 illustrates the quantitative conversion of the amine $-CH_2NH_2$ ($\delta = 3.77$ ppm, P33NH$_2$) to the corresponding Schiff base $-CH_2N{=}CH-$ ($\delta = 4.73$ ppm, P33N=CH-q) and finally to the secondary amine $-CH_2NHCH_2-$ ($\delta = 4.02$, 3.73 ppm, P33-q). These data in collaboration with three new characteristic signals from the 8-hydroxyquinoline moiety prove the successful and quantitative attachment of the 5-aldehyde-8-hydroxyquinoline to the poly(styrene) backbone. Synthesis of Alq$_3$-containing polymers followed the widely employed procedures in the literature and is outlined in Scheme 2.[11] To reduce the extent of polymer cross-linking that is possible via the Alq$_3$ formation between two or three different polymer chains, a large excess of 8-hydroxyquinoline and triethylaluminum were used. Nevertheless, polymer P33-q containing 33% of 8-hydroxyquinoline-functionalized side chains failed to achieve full solubility after Alq$_3$-functionalization. This limited solubility is most likely due to the readily occurrence of interchain cross-linking. However, P10-Alq$_3$ and P10-qAl(qCHO)$_2$ are yellow luminescent solids that are readily soluble in common organic solvents, such as CHCl$_3$, CH$_2$Cl$_2$, and THF. The polymers P10-Alq$_3$ and P10-qAl(qCHO)$_2$ were purified from low molecular weight Alq$_3$ by several cycles of reprecipitations into methanol (Alq$_3$ is readily soluble in MeOH while all polymers are not) until the methanol solution after precipitation is not colored anymore.

The BPh$_2$q-containing polymers, P10-qBph$_2$, P33-qBph$_2$, and P33N=CHqBph$_2$, were obtained in similar fashion as described above for the Alq$_3$-functionalization by the reaction of BPh$_3$ with the 8-hydroxyquinoline-functionalized polymers at room temperature (Scheme 2).[12] In contrast to their aluminum-containing analogues, the boron-based polymers do not exhibit significant interchain cross-linking. Proton NMR spectra that outline the quantitative borylation of P33-q to form P33-

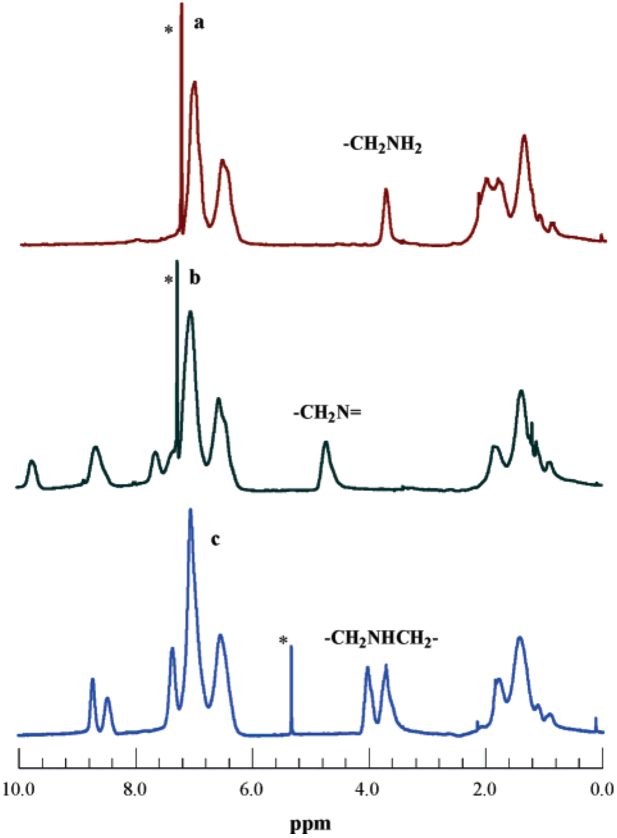


Figure 1. Comparison of the ^{1}H NMR spectra: (a) P33NH$_2$, (b)P33N=CH-q, and (c) P33-q.

Scheme 2. Synthesis of Alq_3 and $qBPh_2$ Pendant Polymers

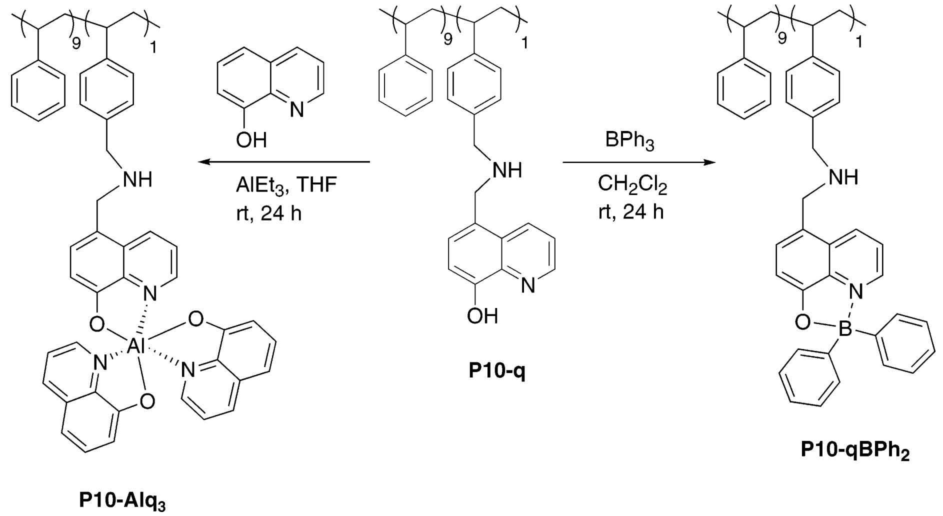


Table 1. Absorption and Emission Data of Polymers[a]

compound	solution absorption[b] λ_{max}, nm	solution emission[b] λ_{max}, nm	thin film emission[c] λ_{max}, nm	$\Phi^{b,d}$	τ, ns
Alq_3	384	517	516	0.09	21
P10-Alq_3	389	516	514	0.04	13
P10qAl$(qCHO)_2$	395	524	511	0.03	
BPh_2q	400	497	489	0.23	32
P10$qBPh_2$	391	497	501	0.20	17
P33$qBPh_2$	395	498	509	0.10	4
P33N=CH$qBPh_2$	407	497	498	0.16	

[a] All polymers were excited at 380 nm. [b] $CHCl_3$ solution at room temperature. [c] Quartz slide at room temperature. [d] Standard: quinine sulfate (= 0.54, 0.1 M H_2SO_4).

$qBPh_2$ are shown in Figure 2. The proton signals of quinolate ($\delta \approx 8.5$ ppm) and two phenyl groups ($\delta \approx 7.2$ and 7.4 ppm) of P33-$qBPh_2$ are identical to those of the respective small molecule $qBPh_2$, which proves the formation of qBph$_2$ moiety on the side chain of P33-q.

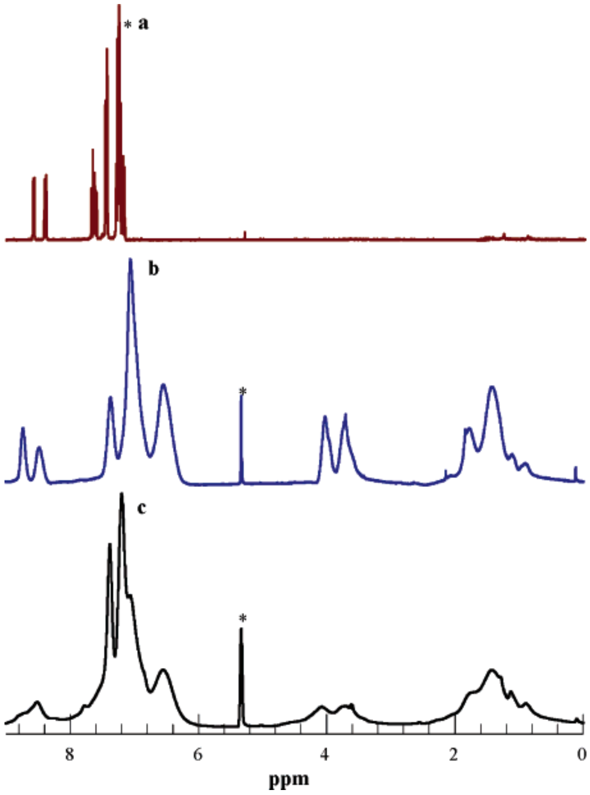


Figure 2. ^1H NMR spectra: (a) $qBPh_2$, (b) P33-q, and (c) P33-$qBPh_2$.

Absorption and Photoluminescence Characterization. Investigations of the absorption and photoluminescence properties of the polymers were carried out in dilute chloroform solutions as well as in the solid films. Thin films of the polymers and the reference compounds Alq_3 and BPh_2q were cast on quartz slides from chloroform solutions. The absorption and emission results are summarized in Table 1.

The absorption and photoluminescent spectra (solution and thin film) of P10-Alq_3 are almost identical to that of the reference compound Alq_3 with the lowest energy absorption maximum and emission maximum at around 390 and 516 nm, respectively (Figures 3−5 and Table 1). These results clearly indicate that the poly(styrene) backbone does not interfere with the photophysical properties of the pendant Alq_3 moiety. The solution absorption and emission of P10-qAl-$(qCHO)_2$ is ≈8 nm red-shifted compared to that of Alq_3. These findings are consistent with previous reports from our group that introduction of electron-withdrawing and/or -donating groups at the 5-position of 8-hydroxyquinoline can tune the emission wavelength.[2] Luminescent quantum yields for P10-Alq_3 and P10-qAl-$(qCHO)_2$ are 0.04 and 0.03, respectively. These quantum yields are slightly lower than the one for the molecular compound Alq_3 ($\Phi = 0.09$) but still acceptable for polymer-supported analogues.

The organoboron quinolate polymers exhibit strong green luminescence in solution and the solid state with emission maxima at around 500 nm and quantum yields of 0.20, 0.10, and 0.16 for P10-$qBPh_2$, P33-$qBPh_2$, and P33N=CH$qBPh_2$, respectively. Their solution and solid emission maxima are very close, suggesting that there are no significant interchain interactions. A comparison with the model compound BPh_2q shows nearly identical

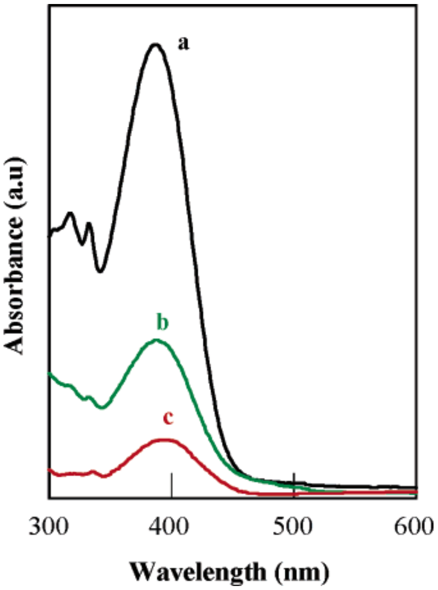


Figure 3. UV−vis absorption spectra in $CHCl_3$: (a) Alq_3, (b) P10-Alq_3, and (c) P10-qAl$(qCHO)_2$.

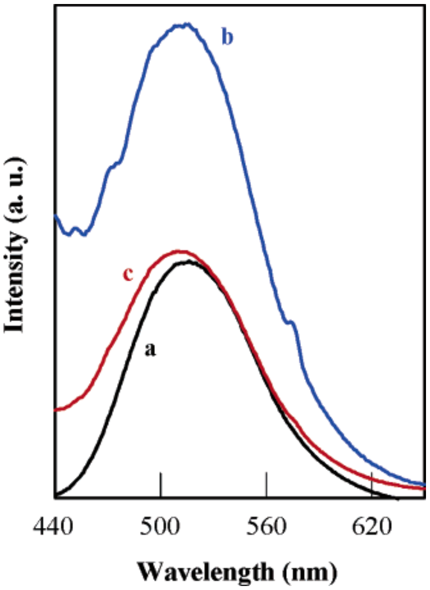


Figure 5. Thin film emission of Alq_3 complexes: (a) Alq_3, (b) P10-Alq_3, and (c) P10-qAl$(qCHO)_2$.

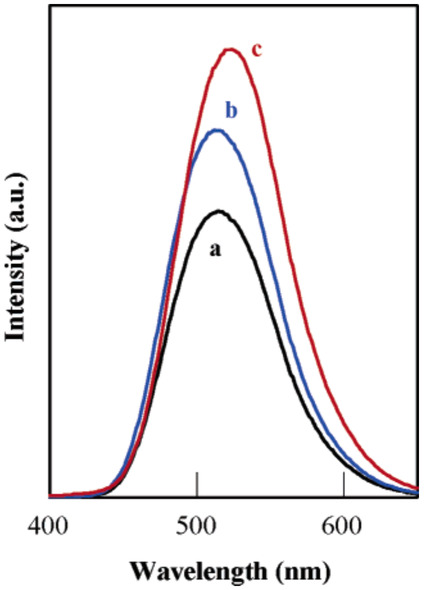


Figure 4. Solution emission of Alq_3 complexes in $CHCl_3$: (a) Alq_3, (b) P10-Alq_3, and (c) P10-qAl$(qCHO)_2$.

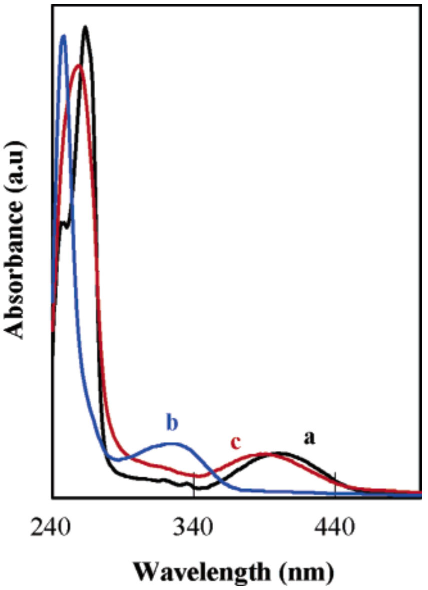


Figure 6. UV−vis absorption spectra in $CHCl_3$: (a) BPh_2q, (b) P10-q, and (c) P10-qBPh_2 in $CHCl_3$.

solution absorption and emission spectra, slightly lower quantum yields, and red-shifted solid-state emissions for the polymeric materials (Table 1, Figures 6−8). These results suggest that there is no significant delocalization of the excited state along the polymer chains.

Luminescence lifetimes of both Alq_3- and BPh_2q-containing polymers are shorter than that of their respective analogues Alq_3 and BPh_2q (Table 1). These results are in agreement with the lower quantum yields of the polymers. For all polymers, their fluorescent decays fit well a single exponential, indicating that luminescent excited states are mainly from the attached Alq_3 and BPh_2q chromophores. The lower luminescent lifetimes and quantum yields of all polymers are likely due to enhanced exciton diffusion to randomly distributed traps within the polymer chains.

In conclusion, we have developed an efficient synthetic approach for the attachment of 8-hydroxyquinoline ligands onto the side chains of poly(styrene) polymers. The resulting polymers can serve as versatile precursors to form a variety of pendant 8-hydroxyquinoline metal complex-based polymers. Alq_3- and BPh_2q-functionalizations were carried out successfully by using these poly(styrene) scaffolds, but other metalated analogues are imaginable. Solution and thin film characterization of these Alq_3- and BPh_2q-containing polymers show luminescent properties similar to those of the respective model compounds, Alq_3 and BPh_2q, suggesting that these materials might be excellent precursors for organic light-emitting diodes.

Experimental Section

Materials and General Methods. Styrene (99%), 4-vinylbenzyl chloride (90%), and chlorobenzene (99%) were purchased from Acros Chemicals and were distilled before use. All other reagents were used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer and a Bruker 400 MHz spectrometer, respectively. UV−vis measurements were obtained on a Shimadzu UV-2401PC recording spectrophotometer. Fluorescence data were obtained

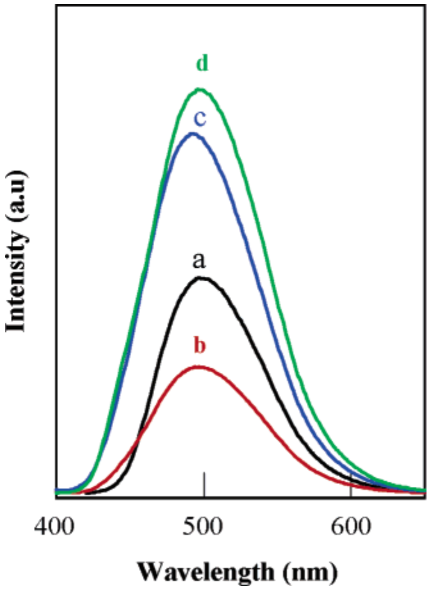


Figure 7. Solution emission of BPh$_2$q complexes in CHCl$_3$: (a) BPh$_2$q, (b) P10-qBPh$_2$, (c) P33-qBPh$_2$, and (d) P33N=CH-qBPh$_2$.

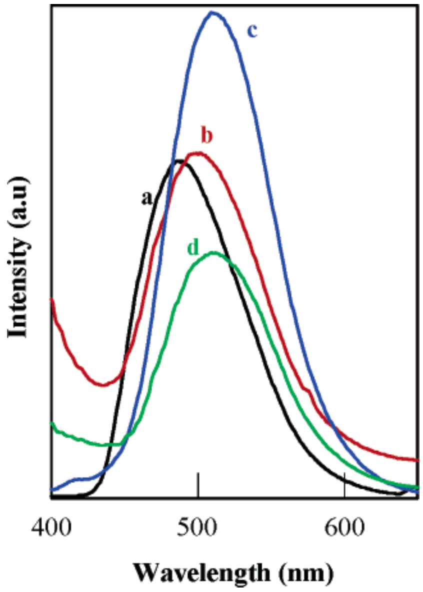


Figure 8. Thin film emission of BPh$_2$q complexes in CHCl$_3$: (a) BPh$_2$q, (b) P10-qBPh$_2$, (c) P33-qBPh$_2$, and (d) P33N=CH-qBPh$_2$.

with a Shimadzu RF-5301PC spectrofluorophotometer. Fluorescence quantum yields were determined relative to quinine sulfate ($\Phi_F = 0.54$ in 0.1 M H_2SO_4).[13] Fluorescence lifetimes were obtained on a PTI model C-72 fluorescence lifetime spectrometer with a PTI GL-3300 nitrogen laser. Gel permeation chromatography measurements were carried out in chloroform (25 °C) with a Shimadzu SCL-10A VP UV−vis detector and two StyragelHMW 6E 7.8 × 300 mm columns. The molecular weights were determined vs poly(styrene) standards. Tris(8-hydroxyquinoline)aluminum (Alq$_3$),[11] 8-hydroxyquinoline biphenylboron (BPh$_2$q),[12] and 5-formyl-8-hydroxyquinoline[14] were prepared according to literature procedures.

Synthesis of Poly(styrene-*p*-chloromethylstyrene), P33Cl. A mixture of *p*-(chloromethyl)styrene (2.00 g, 0.013 mol), styrene (2.72 g, 0.026 mol), AIBN (0.19 g, 1.17 mmol), and 50 mL of chlorobenzene was degassed for 1 h with argon. The reaction mixture was heated at 80 °C for 32 h under an argon atmosphere and then cooled to room temperature. The reaction mixture was poured into an excess of methanol. The resulting white solid was collected by filtration and washed with methanol to remove unreacted monomer and finally dried in air. Yield: 4.01 g (85%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): δ = 0.91−2.09 (broad m, 9H, CH$_2$−CH), 4.55 (broad s, 2H, CH$_2$), 6.10−6.60 (broad m, 6H), 7.09 (broad s, 8H). ^{13}C NMR (100 MHz, CDCl$_3$) (ppm): δ = 26.5, 26.9, 27.9, 40.2, 42.6, 43.7, 125.7, 127.6, 127.9, 134.7, 145.2. GPC: M_n = 6100, M_w = 11 600, and PDI = 1.90. Elem Anal. Calcd for $(C_{25}H_{25}Cl)_n$: C, 83.20%; H, 6.98%; Cl, 9.82%. Found: C, 82.47%; H, 7.01%; Cl, 10.09%.

Synthesis of P10Cl. The same procedure as above was employed. Yield: 90%. ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): δ = 0.90−2.11 (broad m, 30H, CH$_2$−CH), 4.59 (broad s, 2H, CH$_2$), 6.12−7.10 (broad m, 49 H), GPC: M_n = 6400, M_w = 9600, and PDI = 1.50. Elem Anal. Calcd for $(C_{81}H_{81}Cl)_n$: C, 89.26%; H, 7.49%; Cl, 3.25%. Found: C, 88.66%; H, 7.45%; Cl, 3.47%.

Synthesis of Poly(styrene-*p*-(aminomethyl)styrene), P33NH$_2$. Step 1: A solution of P33Cl (1.00 g), potassium phthalimide (1.80 g, 9.73 mmol), and DMF (20 mL) was heated at 100 °C for 12 h. A pink precipitate formed during the reaction. After cooling the reaction to room temperature, the KCl precipitate was filtered off. The filtrate was precipitated into a large volume of methanol, and the resulting white solid was collected by filtration and washed with methanol. Yield: 1.19 g (92%). ^{1}H NMR (CDCl$_3$) (ppm): δ = 0.90−1.75 (broad m, 9H, CH$_2$−CH,), 4.72 (broad s, 2H, CH$_2$), 6.44 (broad s, 6H), 7.02 (broad s, 8H), 7.66 (broad s, phthalimide protons, 2H), 7.81 ppm (broad s, phthalimide protons, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) (ppm): δ = 40.2, 123.1, 125.5, 127.8, 132.0, 133.46, 133.80, 144.94, 167.8.

Step 2: A mixture of the phthalimide derivative (1.00 g) and 1.5 mL of hydrazine monohydrate in 20 mL of ethanol was stirred at reflux for 24 h. A white solid formed as the reaction proceeded. The reaction mixture was filtered and the filtrate was precipitated into a large volume of water. The resulting suspension mixture was kept at 0 °C overnight. Filtration afforded the target amino polymer P33NH$_2$ as a white solid. Yield: 0.54 g (75%). ^{1}H NMR (CDCl$_3$) (ppm): δ = 0.88−1.82 (m, 9H), 3.11 (broad s, NH$_2$), 3.76 (broad s, 2H, CH$_2$), 6.58 (broad s, 6H), 7.26 (broad s, 8H). ^{13}C NMR (100 MHz, CDCl$_3$) (ppm): δ = 27.9, 31.5, 40.3, 46.1, 124.7, 125.6, 127.9, 145.2.

Synthesis of P10NH$_2$. The same procedure as above for the preparation of P33NH$_2$ was employed. Step 1: yield, 87%. Step 2: A mixture of THF and EtOH (1:1, v/v) was used as solvent. Yield: 80%.

Synthesis of P33N=CH-q. A mixture of 5-formyl-8-hydroxyquinoline (0.06 g, 0.34 mmol) and P33NH$_2$ (0.10 g, 0.29 mmol based on repeating units) was dissolved in 40 mL of dry THF and refluxed for 24 h. After cooling, most of the solvent was removed under reduced pressure. The residue was precipitated into a large volume of diethyl ether. The precipitate was collected by filtration to yield the product as a light yellow solid (0.125 g, 85%). ^{1}H NMR (CDCl$_3$) (ppm): δ = 0.90−1.85 (broad m, 9H), 4.73 (broad s, 2H, CH$_2$), 6.59 (broad s, 6H), 7.07 (broad s, 9H), 7.39 (broad s, 1H), 7.66 (broad s, 1H), 8.68 (broad s, 2H), 9.79 (broad s, 1H, CH=N).^{13}C NMR (100 MHz, CDCl$_3$) (ppm): δ = 27.9, 31.9, 40.3, 42.4, 43.8, 46.0, 122.9, 125.6, 127.5, 127.9, 133.5, 135.3, 136.9, 137.8, 145.2, 147.8, 154.2, 161.8.

Synthesis of P10N=CH-q. The same procedure as above for preparation of P33N=CH-q was employed. Yield: 80%.

Synthesis of P33-q. Imine P33N=CH-q (0.06 g, 0.12 mmol based on repeating units) was dissolved in 25 mL of dry methanol, and 1.1 equiv of NaBH$_4$ was added in small increments. After the addition was complete, the solution was allowed to stir for 3 h at room temperature under an Ar atmosphere. The reaction solution was diluted with 100 mL of water and extracted three times with 40 mL of methylene chloride. The combined organic layers were washed with aqueous NaHCO$_3$ solution (0.1 M) and water and dried over Na$_2$SO$_4$. After removal of the majority of the solvent, the residue was precipitated into a large volume of methanol. The precipitate was collected to yield the product as a light yellow solid (0.042 g, 70%). ^{1}H NMR (CD$_2$Cl$_2$) (ppm): δ = 0.90−1.83 (broad m, 9H), 3.73 (broad s, 2H, CH$_2$), 4.02 (broad s, 2H, CH$_2$), 6.55 (broad s, 6H), 7.07 (broad s, 9H), 7.37 (broad s, 2H), 8.48 (broad s, 1H), 8.73 (broad s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): $\delta = 40.3$, 124.6, 125.6, 126.6, 127.9, 129.0, 129.9, 138.6, 145.1.

Synthesis of P10-q. The same procedure as above for preparation of P33-q was employed. A mixture of THF and MeOH (1:1, v/v) was used as solvent. Yield: 65%.

Synthesis of P33-qBPh$_2$. A mixture of P33-q (0.10 g, 0.20 mmol from repeat unit) and BPh_3 (0.05 g, 0.22 mmol) in 25 mL of dry CH_2Cl_2 was stirred for 24 h at room temperature under an Ar atmosphere. After removal of the majority of the solvent, the residue was precipitated into a large volume of hexanes. The precipitate was collected and washed with hexanes to yield the product as a light yellow solid (0.070 g, 52%). ^{1}H NMR ($CDCl_3$) (ppm): $\delta = 0.90-1.83$ (broad m, 9H), 3.75 (broad s, 2H, CH_2), 4.09 (broad s, 2H, CH_2), 6.55 (broad s, 6H), 7.07–7.78 (broad m, 21H), 7.52 (broad s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): $\delta = 40.3$, 109.2, 115.4, 120.2, 123.3, 125.5, 127.4, 127.6, 127.7, 129.6, 131.8, 133.7, 139.1, 140.5, 146.4.

Synthesis of P33N=CH-qBPh$_2$ and P10-qBPh$_2$. The same procedure as above for the preparation of PS33-qBPh$_2$ was employed. Yield: 60% and 65%, respectively.

Synthesis of P10-Alq$_3$. A solution of P10-q (0.05 g) and 8-hydroxyquinoline (0.10 g, 0.68 mmol) in 25 mL of dry THF was added into triethylaluminum (0.22 mL, 0.22 mmol, 1 M in hexanes) via a syringe and stirred at room temperature under an Ar atmosphere for 24 h. During this period, a yellow precipitate, Alq$_3$, was generated. The reaction mixture was filtered to remove any insoluble Alq$_3$. The filtrate was concentrated under reduced pressures and precipitated into a large volume of methanol. The resulting precipitate was collected and dissolved into a small amount of $CHCl_3$ and reprecipitated into methanol. To remove any trace amounts of low molecular weight Alq$_3$, the reprecipitation was repeated several times until the methanol solution was not colored anymore to yield the product as a light yellow solid (0.02 g). ^{1}H NMR ($CDCl_3$) (ppm): $\delta = 0.90-1.83$ (broad m), 3.75 (broad s), 4.09 (broad s), 6.55 (broad s), 7.07 (broad s), 8.23 (broad m), 8.82 (broad m).

Synthesis of P10-qAl(qCHO)$_2$. The same procedure as above for preparation of PS10-Alq$_3$ was employed. ^{1}H NMR ($CDCl_3$) (ppm): $\delta = 0.90-1.83$ (broad m), 3.75 (broad s), 4.09 (broad s), 6.55 (broad s), 7.07 (broad s), 8.23 (broad m), 8.82 (broad m), 9.85 (broad m).

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