Regioregular Head-to-Tail Poly(4-alkylquinoline)s: Synthesis, Characterization, Self-Organization, Photophysics, and Electroluminescence of New n-Type Conjugated Polymers

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Received June 13, 2003; Revised Manuscript Received September 28, 2003

ABSTRACT: Five poly(4-alkylquinoline-2,6-diyl)s (P4AQs), having 100% head-to-tail regioregularity, were synthesized, characterized, and explored as emissive and electron transport materials in polymer light-emitting diodes. The organic solvent (chloroform, tetrahydrofuran, methylene chloride, etc.) soluble poly-(4-alkylquinoline)s had reversible electrochemical reduction with an electron affinity (2.6 eV) that was independent of alkyl chain length. X-ray diffraction studies showed that solution-cast films of regioregular P4AQs have self-organized lamellar structures with an interchain π -stacking distance of 3.9–4.1 Å and an interlayer *d*-spacing that varied linearly from 13.4 Å for butyl to 22.3 Å for tridecyl side chains. The new poly(4-alkylquinoline)s emit blue light at 423–426 nm in dilute chloroform solution and yellow light at 542–557 nm in the solid state. Yellow electroluminescence with a luminance of up to 86 cd/m² and an external quantum efficiency of up to 0.6% was observed for the P4AQs as emissive materials. A large improvement in performance of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene)-based light-emitting diodes (a luminance of up to 700 cd/m² and an external quantum efficiency of up to 3.0%) was observed when the P4AQs were used as the electron transport materials. The new regioregular poly(4-alkylquinoline)s are promising n-type conjugated polymer semiconductors for electronic and optoelectronic devices.

Introduction

Conjugated polymer semiconductors are of growing interest as active elements in electronic and photonic devices including light-emitting diodes,¹⁻³ thin film transistors,^{4,5} photovoltaic cells,^{6,7} and electrochromic cells.⁸ Most of the conjugated polymers that have been widely investigated and explored in these device applications are p-type (electron donor, hole transport) materials exemplified by the polythiophenes, poly-(phenylenevinylene)s, polyfluorenes, and polyphenylenes.^{1–9} n-Type (electron acceptor, electron transport) conjugated polymer semiconductors are also needed for developing improved light-emitting diodes (LEDs), thin film transistors, photovoltaic cells, and other elements of plastic electronics. In the case of field-effect transistors, high electron mobility conjugated polymers are needed for developing n-channel devices essential for designing and producing plastic integrated circuits.^{4,5} Such n-type conjugated polymers having high electron mobility are also essential to achieving high-efficiency solar cells based on bipolar polymer blend or the layered heterojunction architecture.^{6,7} Although a few classes of n-type conjugated polymers, such as the polyquinolines,¹⁰ polyquinoxalines,¹¹ polypyridine,¹² and polybenzobisazoles,^{3h,13} have been explored as electron transport materials in polymer LEDs, the current materials either lack solubility in common organic solvents or are regiorandom and thus lack the ability to self-organize into ordered crystalline thin films.

Regioregular alkylated π -conjugated polymers, exemplified by the regioregular poly(3-alkylthiophene)s, have attracted much recent attention because of their ability to self-organize into highly ordered crystalline films that have shown distinctive electronic and optical properties.¹⁴ It has been shown that regioregular, head-to-tail, poly(3-alkylthiophene)s (P3ATs), which self-order into layered crystalline films, exhibit superior properties, such as better ordering and crystallinity,¹⁴ higher charge carrier mobility,⁴ and enhancement in electrical conductivity when compared to regiorandom analogues. They have found device applications in field-effect transistors⁴ and photovoltaic cells^{6b} due to their high hole mobility resulting from the well-organized lamellar structure in films. Although it can be expected that regioregular n-type π -conjugated polymers will similarly have improved self-ordering and thus higher electron mobility, few such polymers are currently known.^{5,12} A regioregular, head-to-tail, poly(6-hexylpyridine-2,5-diyl) that self-orders into layered crystalline films has been prepared by Yamamoto¹² but is yet to be fully explored as an n-type semiconductor in devices. We have thus been interested in the regiocontrolled synthesis and investigation of new regionegular n-type π -conjugated polymers for electronic device applications.

Many phenylated polyquinolines have been synthesized and extensively investigated due to their high thermal and oxidative stability, outstanding mechanical properties, and optical and electronic properties.^{10,15,16} On the basis of their excellent electron-accepting properties,¹⁵ the phenylated polyguinolines have been extensively explored as emissive and electron transport materials in light-emitting devices.^{3c-h,9} The effects of molecular and supramolecular structures on the electroluminescence and photophysical properties of a series of polyquinolines were also extensively studied.^{3f} However, nearly all of the currently known phenylated polyquinolines are not soluble in aprotic organic solvents unless via complexation,^{10,15,17} thus limiting their use in polymer devices of various architectures.^{3,9} They also lack capacity for self-organization into ordered structures driven by alkyl side chains.



i) R–C–Cl, ZnCl₂, H⁺ ii) Ac₂O, benzene, reflux iii) KMnO₄, HNO₃, 80°C iv) ethanol, NaOH



5 (P4AQ) a. R=n-butyl (P4BQ) b. R=n-hexyl (P4HQ) c. R=n-octyl (P4OQ) d. R=n-decyl (P4DQ) e. R=n-tridecyl (P4TDQ)

In this paper, we report the regiocontrolled synthesis, self-organization, and properties of a series of organic solvent soluble, 100% regioregular, head-to-tail, poly-(4-alkylquinoline)s with various alkyl side chains. Electrochemical redox experiments showed that the new polymers had reversible reduction and photophysical properties that were independent of the alkyl chain length. We find that these polymers can self-organize into layered highly ordered structures in solution-cast solid films. A linear correlation between the interlayer *d*-spacing and the number of carbon atoms in the alkyl side chain was found, confirming that the rigid-rod main chains are spaced by the alkyl side chains. We explored use of the new n-type conjugated polymers in lightemitting diodes (LEDs) as both the emissive and electron transport materials. A large improvement in performance of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-pphenylenevinylene) (MEH-PPV)-based LEDs was observed when the poly(4-alkylquinoline)s were used as the electron transport materials. In a preliminary communication, we reported the synthesis and initial study of two members of the poly(4-alkylquinoline)s, i.e., poly(4-hexylquinoline) and poly(4-octylquinoline).¹⁸

Results and Discussion

Synthesis and Characterization. The synthesis of the monomers (**4a**–**4e**) and their self-polymerization to the corresponding 100% regioregular poly(4-alkylquinoline)s (**5a**–**5e**) are outlined in Scheme 1. The new AB-type monomers **4a**–**4e** were prepared in four steps by modifying a reported method.¹⁹ We ran the third step reaction at 80 °C instead of the reported 60 °C,¹⁹ and we doubled the reaction time. The yield of the first step was moderate, 45–62%. The 87–95% yield of the second step was very good and is much higher than the literature value.¹⁹ The third step involves controlled oxidation of an ethyl group to an acetyl group. Although

 Table 1. Molecular Weights and Thermal Properties of Poly(4-alkylquinoline)s

polymer	yield (%)	$M_{ m w}{}^a$	$M_{\rm w}/M_{\rm n}^a$	$T_{\mathbf{d}}{}^{b}$ (°C)	residual weight ^c (%)
P4BQ	85	d	d	447	67
P4HQ	91	15 150	2.79	460	63
P4OQ	87	10 250	4.02	460	57
P4DQ	90	23 100	3.50	440	54
P4TDQ	90	9 200	2.48	437	36

 a Molecular weights were determined by GPC in chloroform based on polystyrene standards. b Onset decomposition temperature measured by TGA under $N_2.\ ^c$ Residual weights determined by TGA under N_2 up to 900 °C. d No molecular weight was determined due to the incomplete solubility of P4BQ in organic solvents.

the yield of this step is low (25-30%), the reaction is very clean, allowing the starting materials to be readily recovered and reused. The polymers were synthesized by acid-catalyzed Friedländer condensation polymerization with good yields in a range of 85-91%, as shown in Table 1. The molecular structures of poly(4-alkylquinoline)s were confirmed by ¹H NMR, FT-IR, and UV-vis spectra. A representative ¹H NMR spectrum of P4HQ in trifluoroacetic acid-d (CF₃COOD) is shown in Figure 1 (see Supporting Information for other P4AQs). We used CF₃COOD as the NMR solvent because of the overlap of the ¹H NMR chemical shifts of other deuterated solvents such as chloroform-*d* with those of protons in P4AQs. The ¹H NMR spectra were in good agreement with the structures of the polymers. The overall integration ratios between the aliphatic protons and the aromatic protons were consistent with the structures of the polymers. The 100% head-to-tail regioregularity of the P4AQs automatically follows from the AB-type condensation polymerization. In addition, the presence of a nonsplitting peak at 3.74-3.78 ppm, which corresponds to the α -methylene protons of the alkyl groups in head-to-tail linkage, further confirmed the regioregu-



Figure 1. ¹H NMR spectrum of P4HQ in trifluoroacetic acid*d*. Solvent and impurity peaks at 4.0, 6.9, 8.3, and 11.5 ppm.



Figure 2. FT-IR spectra of P4HQ and P4HQ monomer.

lar structures of the P4AQs.^{14c} The singlet peak at 3.05-3.11 ppm in the ¹H NMR spectra of these polymers can be assigned to the terminal acetyl protons in the polymer chains.

The molecular structures of P4AQs were also confirmed by FT-IR spectra. Representative FT-IR spectra of P4HQ and P4HQ monomer are shown in Figure 2. The strong peaks at $1656-1671 \text{ cm}^{-1}$ owing to the carbonyl groups in 4a-4e have almost completely disappeared in the poly(4-alkylquinoline)s. In addition, the two peaks at 3300-3450 cm⁻¹ in the monomers corresponding to primary amines were absent in the FT-IR spectra of the polymers. Instead, new strong bands between 1600 and 1400 cm⁻¹ due to the imine (C=N) group and characteristic of the quinoline ring were observed.^{10a-c} These results confirm the completeness of quinoline ring-forming cyclization. The presence of alkyl side chains in the monomers lowered the reactivity compared to the phenyl-substituted monomers.^{10a-c} Å higher reaction temperature (180 °C) and longer polymerization time was required to get the complete cyclization in poly(4-alkylquinoline)s compared to the 140 °C normally used in the synthesis of phenylated polyquinolines.^{10a-c}

The poly(4-alkylquinoline)s except for P4BQ are soluble in common organic solvents, such as chloroform, THF, and methylene chloride. P4BQ is only partially soluble in chloroform or THF due to its short side chain. As expected, the solubility of P4AQs in common organic solvents increased with the length of the alkyl side chain. The P4AQs are also soluble in protonic acid solvents such as formic acid that are commonly used for phenylated polyquinolines.^{10a-c} The molecular weights



Figure 3. (A) X-ray diffraction patterns of solution-cast films of poly(4-alkylquinoline)s. (B) Interlayer *d*-spacing vs the number of carbons in the alkyl chains.

of P4AQs except P4BQ are summarized in Table 1. We did not do gel permeation chromatography (GPC) of P4BQ because of its incomplete solubility in organic solvents. The remaining P4AQs have moderate weightaverage molecular weights of 9200-23 100 with polydispersity indices (M_w/M_n) of 2.48–4.02 based on polystyrene standards. The absolute number-average molecular weights of P4AQs can also be determined from end-group analysis by ¹H NMR spectroscopy. The number-average molecular weights of the polymers so determined were 3477 (P4BQ), 4853 (P4HQ), 4302 (P4OQ), 5340 (P4DQ), and 4944 (P4TDQ). As shown in Table 1, all the P4AQs possess excellent thermal stability with onset decomposition temperature (T_d) ranging from 437 to 460 °C in nitrogen as revealed in thermogravimetric analysis (TGA). The 5% weight loss temperatures of P4AQs in nitrogen were also in the range 424-464 °C. High residual weights of 36-67% were observed for the series of P4AQs even at 900 °C under N₂. The residual weights of P4AQs decreased with the length of the alkyl side chain. No clear phase transitions were observed in differential scanning calorimetry (DSC) scans of these polymers up to 300 °C.

Self-Organized Structures in Films. Wide-angle X-ray diffraction (WAXD) patterns of films of P4AQs cast from chloroform or formic acid solutions are shown in Figure 3A. The WAXD patterns showed a strong first-order reflection at a 2θ angle of 6.61°, 5.63°, 5.0°, 4.49°, and 3.96° for P4BQ, P4HQ, P4OQ, P4DQ, and P4TDQ, respectively. This first-order reflection can be assigned



Figure 4. Schematic of layered and π -stacking structures of regioregular poly(4-alkylquinoline)s exemplified for poly(4-hexylquinoline).

to the (100) reflection, corresponding to an interlayer *d*-spacing of 13.4, 15.7, 17.7, 19.7, and 22.3 Å for P4BQ, P4HQ, P4OQ, P4DQ, and P4TDQ, respectively. Compared to the regioregular poly(3-alkylthiophene)s,^{14c} the interlayer *d*-spacing is a little shorter in the poly(4alkylquinoline) with the same alkyl side chain. In contrast to the relatively intense WAXD reflections from solution-cast films of P4AQs, very weak and broad firstorder diffractions were observed in the powdered samples of P4AQs. The main reason for this observation is that the macromolecules of P4AQs can self-organize into ordered layered structures more easily on a substrate when the solvent slowly evaporates from the solutioncast films than in the powdered samples. Since the (100) reflections of P4AQs are observed in the out-of-plane scan of X-ray diffraction, we suggest that the highly ordered layered structures in the films of P4AQs are preferentially oriented normal to the substrate. The average crystallite size (L) of P4AQs normal to the (100) planes can be estimated from the width of the (100) reflection peaks by using the Scherrer equation (L = $\lambda/(\beta_0 \cos \theta)$, where λ is wavelength, θ is the Bragg reflection angle, and β_0 is the full width at halfmaxima).²⁰ The estimated mean crystallite size of the P4AQs was 6.1, 7.1, 7.3, 8.4, and 11.2 nm for P4BQ, P4HQ, P4OQ, P4DQ, and P4TDQ, respectively. It appears that a longer alkyl side chain in the P4AQs enhances the interlayer structural order with improvement in the crystallite size. The broad peaks in the diffraction patterns of P4AQs centered at 20.3°-22.4° can be assigned to the (010) reflections, corresponding to a spacing of 3.9-4.1 Å. This side-chain length independent spacing is assigned to the π -stacking distance in the P4AQs. The π -stacking distance in the regioregular poly(4-alkylquinoline)s is thus larger than the 3.6-3.8 Å observed in the regioregular poly(3alkylthiophene)s.14

As shown in Figure 3B, a plot of the interlayer *d*-spacing vs the number of carbon atoms in the alkyl side chain of the P4AQs gives a straight line with a slope of 0.99 Å per carbon atom. The linear correlation clearly indicates that the interlayer *d*-spacing corresponds to a distance between the π -conjugated polymer main chains separated by the alkyl side chains. It is known that there are two common packing modes of alkyl chain substituted polymers, interdigitation and end-to-end packing.²¹ Because the CH₂-ČH₂ group of the planar zigzag conformation of an alkyl chain has an effective distance of 1.25 Å along the alkyl chain axis, we expect the *d*-spacing/carbon atom (slope) to be less than 1.25 Å in the interdigitation model (Figure 4) and between 1.25 and 2.5 Å in the end-to-end model if the tilting of alkyl chain is taken into account. Previous work has

shown that the packing of the alkyl chains in head-totail regioregular poly(3-alkylthiophene)s adopts an endto-end model with a tilting angle of 50°, giving a slope of 1.8 Å per carbon atom for a similar *d*-spacing vs alkyl chain carbon number plot.^{21b} In our case, we concluded that the alkyl chains in head-to-tail regioregular P4AQs interdigitate in view of the observed slope of 0.99 Å per carbon atom and the smaller grafting density of the alkyl chains on the polymer main chain compared to that of poly(3-alkylthiophene)s. The tilting angle of the interdigitated alkyl chains of P4AQs was estimated to be 52° based on the slope (0.99 Å/carbon atom) and the effective length of CH_2-CH_2 group (1.25 Å).

The interdigitation mode of alkyl chain packing in the P4AQs can also be concluded from the results of Figure 3B by the following analysis. An effective distance between the two main chains without any alkyl side chain is estimated to be 9.65 Å from the intercept of the plot in Figure 3B. Therefore, a *d*-spacing of about 17.15 Å (9.65 + 1.25×6 Å) should be observed in P4HQ if the hexyl side chains adopt an interdigitation packing mode. Since a *d*-spacing of 15.7 Å was actually found for P4HQ, the packing of the hexyl chains in P4HQ must be interdigitated with a certain tilt angle. A tilt angle of 52° of the hexyl group in P4HQ was obtained from the experimental *d*-spacing (15.7 Å) and the calculated *d*-spacing (17.15 Å). Similar conclusions were reached for the other P4AQs.

In summary, the X-ray diffraction results clearly show that the new head-to-tail regioregular P4AQs selforganize into layered order structures in which layers of the rigid-rod main chains are spaced by interdigitated and tilted alkyl side chains and have an interchain π -stacking distance of 3.9–4.1 Å within each layer (Figure 4). The alkyl side chains have a tilting angle of 52° in the solution-cast films of poly(4-alkylquinoline)s. Since such self-organized ordered structures are known to facilitate enhanced charge carrier mobility in poly-(3-alkylthiophene)s,¹⁴ we expect the self-organized crystalline thin films of n-type P4AQs to offer good prospects for electron transport in polymer devices. A novel selforganization of the regioregular poly(4-alkylquinoline)s in dilute solutions in protonic acid media was recently discovered and is reported elsewhere.²² Future studies will aim to understand whether any connection exists between the ordered assemblies in solution and the layered films in the solid state.

Photophysical Properties. The optical absorption and photoluminescence (PL) emission spectra of the P4AQs in dilute chloroform solution and in the solid state were obtained. Figure 5 shows the absorption and PL emission spectra of the P4AQs in dilute chloroform solution. All the P4AQs have strong featureless absorption bands and an identical lowest energy $\pi - \pi^*$ transition with a λ_{max} at 385–387 nm (3.2 eV) in dilute solution. Unstructured lowest energy absorption bands are commonly observed in many π -conjugated polymers due to the distribution of conjugation lengths, and thus transition energies, that leads to a broadened absorption and obscured vibronic structure. In addition to the lowest energy $\pi - \pi^*$ transition band, there is an additional higher energy absorption band at 274-276 nm in each solution absorption spectrum of the P4AQ. The solution PL emission spectra of all the P4AQs have wellresolved vibronic structures (Figure 5B) and can thus be assigned to the single-chain or "monomer" emission states of the poly(4-alkylquinoline)s. The P4AQs emit

Table 2. Photophysical and Redox Properties of Poly(4-alkylquinoline)s

	absorption λ_{\max}^a (nm)			emission λ_{\max}^{c} (nm)						
polymer	solution	film	$E_{\rm g}^{{\rm opt}\ b}$ (eV)	solution	film	ϕ_{f} (solution)	$\phi_{\rm f}$ (film)	$E_{\mathrm{red}}^{\mathrm{onset}\ d}\left(\mathrm{V}\right)$	$E_{\rm red}^{o\prime} \ ^{e}$ (V)	EA (eV)
P4BQ	385	400	2.72	423	557	0.22	0.02	-1.77	-1.87	2.63
P4HQ	386	397	2.70	423	547	0.40	0.05	-1.83	-1.95	2.57
P40Q	386	397	2.70	425	547	0.22	0.03	-1.81	-1.95	2.59
P4DQ	386	397	2.71	426	542	0.16	0.02	-1.77	-1.87	2.63
P4TDQ	387	401	2.70	424	551	0.21	0.04	-1.82	-1.92	2.58
PPQ^{f}		414	2.65		578			-1.78	-1.89	2.62

^{*a*} Absorption maxima in solution (chloroform, 10^{-6} mol/L) and as a thin film on silica substrate. ^{*b*} Optical absorption edge gap (E_g^{opt}). ^{*c*} Emission maxima in solution (chloroform, 10^{-6} mol/L) and as a thin film on silica substrate obtained by exciting at absorption λ_{max} . ^{*d*} Onset reduction potentials vs SCE. ^{*e*} Formal reduction potentials. ^{*f*} All the data for PPQ are from refs 3f and 15b.



Figure 5. Optical absorption spectra (A) and PL emission spectra (B) of P4AQs, 5a-5e, in chloroform solution ($\sim 10^{-6}$ M).

blue light with an emission peak at 423-426 nm corresponding to the 0-0 transition in dilute solution. The 0-1 and 0-2 transitions in the PL emission spectra were 454 and 485 nm, respectively. The main photophysical properties of the P4AQs in solution are collected in Table 2.

The absorption spectra of P4AQ thin films are shown in Figure 6A. These absorption spectra of P4AQs in the solid state are very similar to those in solution. The lowest energy $\pi - \pi^*$ transitions are centered at 397– 401 nm (~3.1 eV) while an additional higher energy band is found at 275–279 nm (~4.5 eV) in each spectrum. There is a 12–14 nm red shift in the lowest energy absorption maximum compared to the corresponding spectrum in dilute solution. This is due to an increase in the planarity of the polymer chains and thus an increase in conjugation length in the solid-state resulting from the efficient π -stacking. The solid-state



Figure 6. Optical absorption (A) and PL emission (B) spectra of P4AQs, **5a**–**5e**, as thin films on silica substrates.

 $\pi - \pi^*$ transitions of the P4AQs are slightly blue shifted compared to the phenylated poly(4-phenylquinoline)^{3f} (PPQ, $\lambda_{max} = 414$ nm), indicating a small decrease of electron delocalization along the conjugated backbone as the side group changes from phenyl to alkyl. The absorption spectra of P4AQs with different alkyl chains have identical absorption maxima and spectral shape in dilute solution and in the solid state, showing that the alkyl chain length did not have an effect on the ground-state electronic structures of the P4AQs. The optical band gaps (E_g^{opt}) determined from the absorption edge of the solid-state spectra of the P4AQs are all essentially identical at 2.7 eV, which is a little larger than that of the phenylated derivative PPQ (2.65 eV).

Figure 6B shows the PL emission spectra of P4AQ thin films. They emit yellow light in thin films with PL emission peaks at 542–557 nm. This represents a 20–30 nm blue shift compared to the orange PL emission



Figure 7. Reduction (A) and oxidation (B) cyclic voltammograms of P4AQ (5a-5e) thin films in TBAPF₆/acetonitrile.

from PPQ (578 nm),^{3f} and this is likely an indication of a weaker π -stacking interaction in P4AQs than that in PPQ. The broad, featureless, PL emission bands with a large Stokes shift of about 150 nm (0.8–0.9 eV) in these solid-state PL spectra are clearly due to excimer emission²³ in contrast to the observed single chain emission of the P4AQs in dilute solution. There was no effect of the alkyl chain length on the PL emission spectra of the P4AQs, indicating absence of alkyl chain length effects on the excited-state electronic structures of the P4AQs.

The fluorescence quantum yields (ϕ_f) of P4AQs in dilute chloroform solution and in the solid state are listed in Table 2. The PL quantum yield in solution ranges from 16% for P4DQ to 40% for P4HQ. However, the relative PL quantum efficiency of the P4AQs in the solid state was rather low, 2-5% (based on a thin film of $\sim 10^{-3}$ M 9,10-diphenylanthracene in poly(methyl methacrylate) as a standard ($\phi_f = 83\%$)).^{3f} The poor fluorescence quantum yield in thin films of these polymers is not surprising in view of their efficient π -stacking and emission from intermolecular excimers.²³

Electrochemical Properties. To better understand the electronic structures of the P4AQs in relation to charge injection processes in polymer devices, we performed cyclic voltammetry measurements on films of the P4AQs. The reduction and oxidation cyclic voltammograms of P4AQ thin films are shown in Figure 7. All the poly(4-alkylquinoline)s have reversible reductions with onset reduction potentials of -1.83 to -1.77 V vs SCE.²⁴ The formal reduction potentials were also very similar, being in the range of -1.95 to -1.87 V vs SCE (Table 2).²⁴ We estimated the electron affinity (EA, LUMO level) of the P4AQs to be virtually identical, 2.57-2.63 eV,²⁴ from the onset reduction potentials by taking the SCE energy level to be -4.4 eV below the vacuum level (EA = E_{red}^{onset} + 4.4). If the SCE energy level is instead -4.8 eV, the estimated EA values increase to 3.0 eV. The onset potential, formal potential, and the electron affinity of the P4AQs show little or no change with the alkyl chain length. These redox properties were only slightly changed compared to those of poly(4-phenylquinoline).^{15b} These results suggest that the electrochemical properties of this class of conjugated polymers are determined primarily by the polyquinoline backbone structure. The observed reversible reduction and high electron affinity suggest that the poly(4alkylquinoline)s are intrinsic n-type (electron transport) conjugated polymers similar to the phenylated polyquinolines.3f,15b

However, unlike the phenylated polyquinolines,^{15b} the present alkylated polyquinolines did not have a clear oxidation wave as shown in Figure 7B. A rough estimate of the ionization potential (IP, HOMO level) for the P4AQs (IP = E_{ox}^{onset} + 4.4) from the oxidation cyclic voltammograms is ca. 5.4 eV or greater. Alternatively, the HOMO levels of P4AQs can be obtained from their electron affinities and optical band gaps (IP = EA + E_{g}^{opt}) to be in the range 5.27–5.35 eV. The reversible reduction and absence of clear oxidation suggest that the P4AQs are excellent candidates for n-type doping (electron transport) and hole blocking in devices.

Light-Emitting Diode Properties. Light-emitting diodes (LEDs) based on P4AQs both as emissive and as electron transport materials were fabricated and investigated. We found that the intrinsic electroluminescence (EL) of the poly(4-alkylquinoline)s in single-layer ITO/ PEDOT/**5b**-**5e**/Al type devices was very weak with a luminance of 4-21 cd/m². Yellow electroluminescence with an emission peak at 550-552 nm was observed in four of the P4AQs, **5b-5e**. P4BQ (**5a**) did not show EL emission in a single-layer device. The EL spectra of P4HQ, P4OQ, and P4TDQ are shown in Figure 8A. The EL emission spectra are nearly identical to PL emission spectra, and this means that the P4AQs function as emissive materials in these diodes. This also means that the EL emission is from intermolecular excimers as shown for the PL spectra. The turn-on voltage of the devices was high at 12.5–15 V. The corresponding external quantum efficiency (EQE) was very low, 0.003-0.008% (Table 3).

The difference between the IP of PEDOT (5.1 eV) and the estimated IP of the P4AQs (~5.3-5.4 eV) and the imbalanced charge transport in the P4AQs account for the poor performance of these polymers as emissive materials in LEDs. Therefore, poly(N-vinylcarbazole) (PVK) with an IP of 5.8 eV²⁵ was inserted between PEDOT and P4HQ (or P4OQ) as a hole injection and hole transport layer in the LEDs. Yellow electroluminecence with an emission peak at 552 nm, which is identical to the broad, featureless, PL spectra, was again observed for both P4HQ and P4OQ in LEDs of the type ITO/PEDOT/PVK/P4HQ(or P4OQ)/Al. This indicates that the EL emission from these devices comes from only the P4AQ layer. The current-voltage and luminancevoltage curves of these bilayer LEDs with emissive P4HQ or P4OQ are shown in Figure 8B. The diodes had a turn-on voltage of 5 V and a luminance of 69-86 cd/

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LED configuration	turn-on voltage (V)	$L_{\rm max}^a$ (cd/m ²)	$J_{\max}{}^{b}$ (mA/cm ²)	$V_{\max}{}^{c}$ (V)	EQE^{d} (%)			
P4BQ								
P4HQ	12.5	21	116	20.0	0.007			
P4OQ	14	12	84	20.0	0.005			
P4DQ	15	4	39	20.0	0.003			
P4TDQ	14	9	37	21.0	0.008			
PVK/P4HQ	5	86	246	10	0.6			
PVK/P4OQ	5	69	224	10	0.22			
MEH-PPV	4	66	500	7.5	0.03			
MEH-PPV/P4BQ	10	245	248	23	0.043			
MEH-PPV/P4HQ	5	700	210	13	0.56			
					3.0 (10 V)			
MEH-PPV/P4OQ	5	528	206	10.0	0.51			
MEH-PPV/P4DQ	9.0	392	316	21.5	0.07			
MEH-PPV/P4TDQ	9.5	312	439	14.0	0.055			

Table 3. Electroluminescent Device Properties of Poly(4-alkylquinoline)s

^a Maximum luminance. ^b Maximum current. ^c Maximum voltage. ^d External quantum efficiency.



Figure 8. (A) EL spectra of P4HQ (**5b**), P4OQ (**5c**), and P4TDQ (**5e**). (B) Current–voltage and luminance–voltage characteristics of ITO/PEDOT/PVK/**5b** (or **5c**)/Al LEDs.

 m^2 at 10 V. The external quantum efficiency was 0.6% for P4HQ and 0.22% for P4OQ. These results suggest that the device performance (luminance, turn-on voltage, and EQE) can be substantially improved by finding an optimum hole injection and transport layer for P4AQ LEDs. Although these P4AQ LEDs are not optimized, the low device performance when they are used as emissive EL materials is consistent with their low solidstate PL quantum yields. Because of their large ionization potentials, high electron affinities, and poor solidstate PL quantum yields, the poly(4-alkylquinoline)s are thus more promising as hole blocking and electron transport materials that could be used in conjunction with other more emissive conjugated polymers for the construction of multilayer or blend LEDs.^{2,3,9}

The electron transport and hole blocking properties of all the P4AQs were investigated in layered LEDs of the type ITO/PEDOT/MEH-PPV/5a-5e/Al, where MEH-PPV was used as the emissive and hole transport layer. The EL spectra of these layered LEDs are shown in Figure 9A along with the EL spectrum of a singlelayer MEH-PPV diode. The EL spectra of bilayer MEH-PPV/P4AQ diodes, with an EL emission maximum at 583-594 nm, are nearly identical with that of the single-layer MEH-PPV diode (579 nm). These EL spectra clearly show that MEH-PPV acts as the emitting layer, and P4AQ functions as an electron transport and a hole blocking material in these bilayer devices. We note that the EL spectra of the ITO/PEDOT/MEH-PPV/P4BQ (or P4DQ)/Al diodes showed a small blue shift in emission maximum (~ 10 nm) when the applied bias voltage was increased from 10 to 22 V (not shown). This could be an indication that a small portion of the EL emission in these diodes comes from P4BQ or P4DQ at high bias voltages (over 20 V). No such blue shift was observed in bilayer devices using the other P4AQs.

The performance of the layered MEH-PPV/P4AQ LEDs was found to be greatly enhanced by the introduction of P4AQ as the electron transport layer. The luminance-voltage and current-voltage characteristics of these MEH-PPV/P4AQ diodes are shown in Figure 9B,C. These LEDs showed bright orange-red EL emission with a turn-on voltage of 5-10 V and a luminance of 245–700 cd/m² at $10-\bar{2}3$ V, whereas the single-layer MEH-PPV diode had a turn-on voltage of 4 V and a luminance of 66 cd/m² at 7.5 V (Table 3). The maximum external quantum efficiency of the layered devices varied from 0.043% for P4BQ to 3.0% for P4HQ. This represents a factor of 100 enhancement in EL device efficiency when using P4HQ as an electron transport material for MEH-PPV-based LEDs. In the case of MEH-PPV/P4OQ LEDs, the enhancement in EL external quantum efficiency was 17 times compared to the single-layer MEH-PPV diodes. Thus, the use of P4AQs as electron transport materials in MEH-PPV-based LEDs has resulted in substantial enhancement in the LED performance. We expect that the poly(4-alkylquinoline)s could also be used as electron transport materials for other electroluminescent polymers including arylene vinylene polymers and polyfluorenes.

Conclusions

Novel poly(4-alkylquinoline)s with 100% head-to-tail regioregularity have been synthesized by self-condensation polymerization of new AB-type monomers. Wideangle X-ray diffraction studies showed that solution-



Figure 9. (A) EL spectra, (B) luminance–voltage characteristics, and (C) current–voltage characteristics of ITO/PEDOT/ MEH–PPV/P4AQ(**5a–5e**)/Al diodes and a single-layer MEH– PPV diode.

cast films of the regioregular poly(4-alkylquinoline)s have highly ordered, self-organized, π -stacked lamellar structures in which the packing of the alkyl side chains takes an interdigitation mode with a tilting angle of about 52°. The poly(4-alkylquinoline)s emit blue light in dilute solutions and exhibit yellow photoluminescence and electroluminescence in the solid state. Initial use of the new n-type polymers as electron transport materials in MEH–PPV-based LEDs has resulted in a large enhancement in the device performance (a luminance of up to 700 cd/m² and an external quantum efficiency of up to 3.0%), demonstrating that they are promising electron transport materials for polymer LEDs.

Experimental Section

Materials. Valeryl chloride, heptanoyl chloride, nonanoyl chloride, myristoyl chloride, 4-ethylaniline, zinc chloride, hydrochloric acid, methylene chloride, acetic anhydride, potassium permanganate, magnesium oxide, nitric acid, ethanol, diphenyl phosphate (DPP), poly(ethylenedioxythiophene)/poly(styrenesulfonic acid) (PEDOT; solution in water), and poly-(*N*-vinylcarbazole) (PVK) were used as received from Aldrich. Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH–PPV, $M_w \sim 85$ 000) was purchased from American Dye Source, Inc. Undecanoyl chloride was used as received from TCI. *m*-Cresol was purified by distillation under reduced pressure.

Monomer Synthesis. 1-(5-Acetyl-2-aminophenyl)pentan-1-one (**4a**), 1-(5-acetyl-2-aminophenyl)heptan-1-one (**4b**), 1-(5acetyl-2-aminophenyl)nonan-1-one (**4c**), 1-(5-acetyl-2-aminophenyl)undecan-1-one (**4d**), and 1-(5-acetyl-2-aminophenyl)tetradecan-1-one (**4e**) were synthesized in four steps by modifying a reported method,¹⁹ as shown in Scheme 1.

1-(2-Amino-5-ethylphenyl)pentan-1-one (1a). To a stirred solution of 10.2 g (0.073 mol) of zinc chloride in 24.3 g (0.202 mol) of valeryl chloride maintained at 120 °C, 6.1 g (0.05 mol) of 4-ethylaniline was added in portions. The resulting mixture was refluxed at 180 °C for 2 h. After cooling to 135 °C, 80 mL of 9 M hydrochloric acid was slowly added in portions, and the mixture was stirred and refluxed at 135 °C for 25 h. After the mixture was cooled to 35 °C, 80 mL of methylene chloride was added, followed by about 80 mL of water. The mixture was extracted with CH2Cl2, and the organic layer was sequentially washed with 3 M aqueous hydrochloric acid solution, 3 M aqueous sodium hydroxide solution, and water. The organic layer was dried over sodium sulfate, filtered, and evaporated under vacuum, yielding a dark viscous oil. The crude product was purified on silica gel column (10% ethyl acetate in hexane as eluent) to yield 6.4 g of compound 1a (62%) of yellow needles; mp 58.2–58.9 °C. $^1\rm H$ NMR (500 MHz, CDCl_3): δ 7.55 (s, 1H), 7.14 (d, 1H), 6.68 (d, 1H), 2.93 (t, 2H), 2.54 (m, 2H), 1.69 (m, 2H), 1.35 (m, 2H), 1.19 (t, 3H), 0.93 (t, 3H).

N-(4-Ethyl-2-pentanoylphenyl)acetamide (2a). Acetic anhydride (5.77 mL, 61.2 mmol) was added to a solution of **1a** (6 g, 29.3 mmol) in 100 mL of benzene, and the solution was refluxed for 2 h. The solvent was evaporated to yield a light yellow solid. The obtained solid was dissolved in methylene chloride, washed with 10% aqueous NaOH solution and water, and dried over sodium sulfate. The solvent was evaporated to afford a light yellow solid. The crude product was purified by flash column chromatography (silica gel, 15% ethyl acetate in hexane), and compound **2a** (6.9 g) was obtained as a white solid with 95% yield; mp 51.1−52.5 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.63 (d, 1H), 7.72 (s, 1H), 7.40 (d, 1H), 3.03 (t, 2H), 2.67 (m, 2H), 2.23 (s, 3H), 1.72 (m, 2H), 1.44 (m, 2H), 1.26 (t, 3H), 0.99 (t, 3H).

N-(4-Acetyl-2-pentanoylphenyl)acetamide (3a). A threenecked flask was charged with 3 g (75 mmol) of magnesium oxide, 10 mL (217 mmol) of concentrated nitric acid, and 700 mL of water. To the resulting solution, 6.9 g (28 mmol) of 2a and 11.6 g (73 mmol) of potassium permanganate were added. The reaction mixture was heated with stirring (magnetic bar) at 80 °C for 10 h. After cooling to room temperature, the solution was purged with a stream of gaseous sulfur dioxide to dissolve the manganese dioxide. The aqueous layer of the reaction mixture was extracted with methylene chloride, washed with water, and dried over sodium sulfate. After evaporating the solvent, the crude product was purified by flash column chromatography (silica gel, 30% ethyl acetate in hexane) to afford compound 3a (1.82 g) as colorless needles with 25% yield; mp 91.0-91.9 °C. 3.2 g of 2a was recovered. ¹H NMR (500 MHz, CDCl₃): δ 8.85 (d, 1H), 8.60 (s, 1H), 8.07 (d, 1H), 3.11 (t, 2H), 2.63 (s, 3H), 2.25 (s, 3H), 1.74 (m, 2H), 1.42 (m, 2H), 0.98 (t, 3H).

1-(5-Acetyl-2-aminophenyl)pentan-1-one (4a). To a solution of **3a** (1.8 g, 6.9 mmol) in 60 mL of ethanol was added 35 mL (69.2 mmol) of 2 M aqueous NaOH. The reaction mixture was refluxed for 1 h. After the ethanol was evaporated,

the aqueous layer was extracted with methylene chloride, washed with water, and dried over sodium sulfate. The obtained yellow solid was purified by flash column chromatography (silica gel, 30% ethyl acetate in hexane), followed by recrystallization from ethanol to afford compound **4a** (1.28 g) as light yellow needles with 85% yield; mp 88.0–88.9 °C. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.30; H, 7.83; N, 6.35. ¹H NMR (500 MHz, CDCl₃): δ 8.48 (s, 1H), 7.86 (d, 1H), 6.65 (d, 1H), 3.02 (t, 2H), 2.52 (s, 3H), 1.74 (m, 2H), 1.43 (m, 2H), 0.98 (t, 3H). FT-IR (KBr, cm⁻¹): 3427, 3315, 2952, 2872, 1671, 1601, 1488, 1370, 1253, 1170, 962, 824, 664.

1-(2-Amino-5-ethylphenyl)heptan-1-one (1b). This compound was prepared by a procedure similar to that of **1a**, using heptanoyl chloride instead of valeryl chloride. Compound **1b** (10 g) was obtained as a yellow viscous oil with 52% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.56 (s, 1H), 7.14 (d, 1H), 6.62 (d, 1H), 6.15 (s, 2H), 2.95 (t, 2H), 2.58 (m, 2H), 1.74 (m, 2H), 1.35 (m, 6H), 1.22 (t, 3H), 0.92 (t, 3H).

N-(4-Ethyl-2-heptanoylphenyl)acetamide (2b). This compound was prepared by a procedure similar to that of 2a and obtained as a colorless viscous oil with 95% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.63 (d, 1H), 7.72 (s, 1H), 7.40 (d, 1H), 3.03 (t, 2H), 2.67 (m, 2H), 2.23 (s, 3H), 1.73 (m, 2H), 1.36 (m, 6 H), 1.26 (t, 3H), 0.92 (t, 3H).

N-(4-Acetyl-2-heptanoylphenyl)acetamide (3b). This compound was prepared by a procedure similar to that of **3a** and was isolated as colorless needles with 25% yield; mp 78.2–78.9 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.85 (d, 1H), 8.60 (s, 1H), 8.09 (d, 1H), 3.11 (t, 2H), 2.62 (s, 3H), 2.27 (s, 3H), 1.76 (m, 2H), 1.37 (m, 6H), 0.93 (t, 3H).

1-(5-Acetyl-2-aminophenyl)heptan-1-one (4b). Compound **4b** was prepared by a procedure similar to that of **4a** and obtained as light yellow needles with 90% yield; mp 82.1–82.6 °C. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.76; H, 8.55; N, 5.65. ¹H NMR (500 MHz, CDCl₃): δ 8.48 (s, 1H), 7.86 (d, 1H), 6.82 (broad, 2H), 6.65 (d, 1H), 3.02 (t, 2H), 2.53 (s, 3H), 1.74 (m, 2H), 1.35 (m, 6H), 0.91 (t, 3H). FT-IR (KBr, cm⁻¹): 3427, 3314, 2947, 2864, 1663, 1605, 1493, 1364, 1232, 1187, 967, 830, 666.

1-(2-Amino-5-ethylphenyl)nonan-1-one (1c). This compound was prepared by a procedure similar to that of **1a** and isolated as a light yellow oil with 56% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.56 (s, 1H), 7.14 (d, 1H), 6.63 (d, 1H), 6.15 (s, 2H), 2.95 (t, 2H), 2.58 (m, 2H), 1.74 (m, 2H), 1.32 (m, 10H), 1.23 (t, 3H), 0.91 (t, 3H).

N-(4-Ethyl-2-nonanoylphenyl)acetamide (2c). This compound was prepared by a procedure similar to that of **2a** and obtained as white needles with 93% yield; mp 39.3–40.0 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.65 (d, 1H), 7.72 (s, 1H), 7.41 (d, 1H), 3.03 (t, 2H), 2.68 (m, 2H), 2.22 (s, 3H), 1.74 (m, 2H), 1.30 (m, 10H), 1.27 (t, 3H), 0.91 (t, 3H).

N-(4-Acetyl-2-nonanoylphenyl)acetamide (3c). This compound was prepared by a procedure similar to that of **3a** and obtained as colorless needles with 27% yield; mp 79.5–80.2 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.87 (d, 1H), 8.62 (s, 1H), 8.11 (d, 1H), 3.13 (t, 2H), 2.64 (s, 3H), 2.30 (s, 3H), 1.78 (m, 2H), 1.32 (m, 10H), 0.89 (t, 3H).

1-(5-Acetyl-2-aminophenyl)nonan-1-one (4c). Compound **4c** was prepared by a procedure similar to that of **4a** and obtained as light yellow needles with 92% yield; mp 72.4–73.2 °C. Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.04; H, 9.02; N, 5.06. ¹H NMR (500 MHz, CDCl₃): δ 8.50 (s, 1H), 7.87 (d, 1H), 6.81 (broad, 2H), 6.68 (d, 1H), 3.03 (t, 2H), 2.56 (s, 3H), 1.74 (m, 2H), 1.30 (m, 10H), 0.91 (t, 3H). FT-IR (KBr, cm⁻¹): 3445, 3332, 2920, 2865, 1656, 1607, 1495, 1375, 1254, 1182, 977, 830, 667.

1-(2-Amino-5-ethylphenyl)undecan-1-one (1d). Compound **1d** was prepared by a procedure similar to that of **1a** and isolated as a light yellow solid with 45% yield; mp 40.8–42.2 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.56 (s, 1H), 7.14 (d, 1H), 6.63 (d, 1H), 6.14(broad, 2H), 2.95 (t, 2H), 2.58 (m, 2H), 1.74 (m, 2H), 1.30 (m, 14H), 1.23 (t, 3H), 0.90 (t, 3H).

N-(**4**-**Ethyl-2**-**undecanoylphenyl)acetamide (2d).** Compound **2d** was prepared by a procedure similar to that of **2a**

and obtained as white needles with 88% yield; mp 46.6–47.4 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.65 (d, 1H), 7.72 (s, 1H), 7.41 (d, 1H), 3.03 (t, 2H), 2.68 (m, 2H), 2.23 (s, 3H), 1.74 (m, 2H), 1.30 (m, 14H), 1.27 (t, 3H), 0.90 (t, 3H).

N-(4-Acetyl-2-undecanoylphenyl)acetamide (3d). Compound 3d was prepared by a procedure similar to that of 3a and obtained as colorless needles with 24% yield; mp 62.1–64 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.87 (d, 1H), 8.62 (s, 1H), 8.11 (d, 1H), 3.13 (t, 2H), 2.64 (s, 3H), 2.29 (s, 3H), 1.75 (m, 2H), 1.30 (m, 17H), 0.90 (t, 3H).

1-(5-Acetyl-2-aminophenyl)undecan-1-one (4d). This compound was prepared by a procedure similar to that of **4a** and obtained as light yellow needles with 92% yield; mp 67.9–68.6 °C. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. Found: C, 75.26; H, 9.24; N, 4.64. ¹H NMR (500 MHz, CDCl₃): δ 8.49 (s, 1H), 7.87 (d, 1H), 6.67 (d, 1H), 3.03 (t, 2H), 2.56 (s, 3H), 1.75 (m, 2H), 1.30 (m, 17H), 0.90 (t, 3H). FT-IR (KBr, cm⁻¹): 3444, 3332, 2920, 2851, 1657, 1606, 1496, 1376, 1265, 1242, 1183, 978, 828, 668.

1-(2-Amino-5-ethylphenyl)tetradecan-1-one (1e). Compound **1e** was prepared by a procedure similar to that of **1a** and isolated as a colorless solid with 50% yield; mp 51.9–52.8 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.58 (s, 1H), 7.16 (d, 1H), 6.70 (d, 1H), 5.58 (broad, 2H), 2.96 (t, 2H), 2.59 (m, 2H), 1.73 (m, 2H), 1.24 (m, 23H), 0.90 (t, 3H).

N-(4-Ethyl-2-tetradecanoylphenyl)acetamide (2e). Compound **2e** was prepared by a procedure similar to that of **2a** and obtained as white needles with 87% yield; mp 49.5–50.8 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.65 (d, 1H), 7.71 (s, 1H), 7.41 (d, 1H), 3.03 (t, 2H), 2.68 (m, 2H), 2.22 (s, 3H), 1.74 (m, 2H), 1.26 (m, 23H), 0.90 (t, 3H).

N-(4-Acetyl-2-tetradecanoylphenyl)acetamide (3e). Compound **3e** was prepared by a procedure similar to that of **3a** and obtained as colorless needles with 25% yield; mp 96.6–97.3 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.87 (d, 1H), 8.62 (s, 1H), 8.11 (d, 1H), 3.11 (t, 2H), 2.64 (s, 3H), 2.29 (s, 3H), 1.74 (m, 2H), 1.30 (m, 23H), 0.90 (t, 3H).

1-(5-Acetyl-2-aminophenyl)tetradecan-1-one (4e). This compound was prepared by a procedure similar to that of **4a** and obtained as light yellow needles with 90% yield; mp 83.6–84.4 °C. Anal. Calcd for C₂₂H₃₅NO₂: C, 76.47; H, 10.21; N, 4.05. Found: C, 76.39; H, 10.24; N, 3.96. ¹H NMR (500 MHz, CDCl₃): δ 8.49 (s, 1H), 7.87 (d, 1H), 6.66 (d, 1H), 3.03 (t, 2H), 2.56 (s, 3H), 1.74 (m, 2H), 1.32 (m, 23H), 0.90 (t, 3H). FT-IR (KBr, cm⁻¹): 3407, 3307, 2920, 2850, 1658, 1611, 1472, 1364, 1227, 1178, 967, 848, 720, 667.

Polymer Synthesis. The synthesis of the regioregular poly-(4-alkylquinoline-2,6-diyl)s (**5a**–**5e**) is shown in Scheme 1.

Poly(4-butylquinoline-2,6-diyl) (P4BQ, 5a). 1-(5-Acetyl-2-aminophenyl)pentan-1-one (4a, 800 mg, 3.65 mmol) was added to a solution of 1.5 g of diphenyl phosphate (DPP) and 3 g of freshly distilled *m*-cresol in a cylindrical reaction flask fitted with a mechanical stirrer, a gas inlet, and two sidearms. The reactor was purged with argon for 20 min before the temperature was raised slowly to 70 °C. The reaction was run at this temperature for 1 h. The temperature was then raised slowly to 180 °C within 6 h and maintained for 5 days under static argon. As the viscosity of the reaction mixture increased with time, additional *m*-cresol was added to the reaction mixture to facilitate efficient stirring. Thereafter, the reaction was quenched by cooling it down to room temperature under argon and precipitating it in 300 mL of 10% triethylamine/ ethanol solvent mixture. The precipitated polymer was collected by suction filtration and purified by Soxhlet extraction with 10% triethylamine/ethanol mixture for 48 h. The polymer was dried under vacuum at 60 °C for 24 h to give a dark red solid (582 mg, 87%). ¹H NMR (300 MHz, CF_3COOD): δ 9.38 (s, 1H), 8.92 (s, 2H), 8.60 (s, 1H), 3.78 (s, 2H), 3.11 (s, terminal acetyl protons), 2.12 (s, 2H), 1.76 (s, 2H), 1.19 (s, 3H). FT-IR (film, cm⁻¹): 2955, 2929, 2870, 1593, 1557, 1468, 1427, 1341, 1244, 881, 843.

Poly(4-hexylquinoline-2,6-diyl) (P4HQ, 5b). This polymer was prepared by a procedure similar to that of **5a** and isolated as an orange solid with 91% yield. ¹H NMR (300 MHz, CF₃COOD): δ 9.39 (s, 1H), 8.92 (s, 2H), 8.60 (s, 1H), 3.77

(broad, 2H), 3.11 (s, terminal acetyl protons), 2.16 (broad, 2H), 1.50 (broad, 6H), 1.01 (s, 3H). FT-IR (film, cm⁻¹): 2927, 2857, 1593, 1558, 1508, 1466, 1340, 1234, 881, 842.

Poly(4-octylquinoline-2,6-diyl) (P4OQ, 5c). This polymer was prepared by a procedure similar to that of **5a** and obtained as an orange solid with 87% yield. ¹H NMR (300 MHz, CF₃-COOD): δ 9.37 (s, 1H), 8.91 (s, 2H), 8.59 (s, 1H), 3.76 (broad, 2H), 3.09 (s, terminal acetyl protons), 2.14 (broad, 2H), 1.39 (broad, 10H), 0.94 (s, 3H). FT-IR (film, cm⁻¹): 2925, 2854, 1593, 1558, 1510, 1467, 1340, 1234, 880, 842.

Poly(4-decylquinoline-2,6-diyl) (P4DQ, 5d). P4DQ was prepared by a procedure similar to that of **5a** and isolated as a yellow solid with 90% yield. ¹H NMR (300 MHz, CF₃-COOD): δ 9.28 (s, 1H), 8.79 (s, 2H), 8.51 (s, 1H), 3.74 (broad, 2H), 3.05 (s, terminal acetyl protons), 2.07 (broad, 2H), 1.31 (broad, 14H), 0.85 (s, 3H). FT-IR (film, cm⁻¹): 2924, 2853, 1593, 1557, 1511, 1469, 1342, 1233, 881, 842.

Poly(4-tridecylquinoline-2,6-diyl) (P4TDQ, 5e). This polymer was prepared by a procedure similar to that of **5a** and isolated as a yellow solid with 90% yield. ¹H NMR (300 MHz, CF₃COOD): δ 9.38 (s, 1H), 8.91 (s, 2H), 8.61 (s, 1H), 3.78 (broad, 2H), 3.10 (s, terminal acetyl protons), 2.17 (broad, 2H), 1.39 (broad, 20H), 0.94 (s, 3H). FT-IR (film, cm⁻¹): 2929, 2858, 1596, 1564, 1468, 1340, 1300, 1237, 885, 845.

Characterization. FT-IR spectra were taken on a Perkin-Elmer 1720 FTIR spectrophotometer with KBr pellets or NaCl plates. ¹H NMR spectra were recorded on a Bruker-DRX499 or Bruker-AF301 spectrometer at 500 and 300 MHz, respectively. Melting points were determined on an Electrothermal IA9100 digital melting point instrument at a heating rate of 1 °C/min. Gel permeation chromatography (GPC) analysis of the polymers was performed on an AM PGC gel column with Knauer DRI 8X detector, using chloroform as eluent and polystyrene standards as reference. Differential scanning calorimetry (DSC) analysis was performed on a TA instrument Q100 under N₂ at a heating rate of 10 °C/min, and thermogravimetric analysis (TGA) was conducted with a TA instrument Q50 at a heating rate of 20 °C/min under a nitrogen gas flow. Elemental analysis was performed by Oneida Research Services, Inc. (Whitesboro, NY).

Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Philips PW 1830 X-ray diffractometer. The X-ray beam was a nickel-filtered Cu K α (λ = 1.5418 Å) radiation. Data were obtained from 3° to 30° (2 θ) at a scan rate of 1°/min. WAXD measurements were performed on films of the polymers cast from 1 to 1.5 wt % solutions in chloroform or formic acid onto Si substrate, and the solvent was evaporated in air. UV-vis spectra were recorded on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer. Photoluminescence spectra were measured on a PTI QuantaMaster model C-60/2000 spectrofluorometer (Photon Technology International Inc.). Fluorescence quantum yields in solution were determined by using a perylene standard (10⁻⁶ M in chloroform, $\Phi_f = 87\%$).²⁶ Approximate relative fluorescence quantum efficiencies of the polymer thin films were determined by using a thin film of $\sim 10^{-3}$ M 9,10-diphenylanthracene in poly(methyl methacrylate) as a standard ($\phi_f = 83\%$).^{3f} Cyclic voltammetry measurements were performed on an EG&G Princeton Applied Research potentiostat/galvanostat instrument (model 273A) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile. Platinum (Pt) wire electrodes were used as both counter and working electrodes, and the Ag/Ag⁺ electrode (Bioanalytical System, Inc.) was used as the reference. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an internal standard, and the potential values, thus, obtained in reference to the Ag/Ag⁺ electrode were converted to the saturated calomel electrode (SCE) scale. The films of P4AQs (5a-5e) were coated onto the Pt working electrode by dipping the Pt wire into 0.5-1 wt % chloroform or formic acid solutions and dried under vacuum at 80 °C for 6 h.

Fabrication and Characterization of LEDs. The devices, ITO/PEDOT/P4AQ/Al, ITO/PEDOT/PVK/P4HQ or P4OQ/Al, and ITO/PEDOT/MEH-PPV/P4AQ/Al, were fabricated by sequential spin-coating of the polymer layers onto a precleaned

ITO-coated glass substrate. Electroluminescence (EL) spectra were measured on a PTI QuantaMaster model C-60/2000 spectrofluorometer (Photon Technology International Inc.). The electrical characteristics of the devices were measured on an HP4155A semiconductor parameter analyzer together with a Grasby S370 optometer equipped with a calibrated luminance sensor head. The EL quantum efficiencies of the diodes were determined by using procedures similar to those previously reported.^{3f} More details of our device fabrication and characterization can be found in our previous reports.^{3c-h,9} All the fabrications and measurements were done under ambient laboratory conditions.

Acknowledgment. This work was supported by the Army Research Office TOPS MURI (DAAD19-01-1-0676), the Air Force Office of Scientific Research (F49620-03-1-0162), and in part by the Office of Naval Research.

Supporting Information Available: ¹H NMR spectra, FT-IR spectra, and TGA thermograms of the poly(4-alkylquinoline)s (P4AQs). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0348021