Research Paper **Engineering**

Photophysical and Elecroluminescent Properties of PQ

Pratima V.Damre	Government College of Engineering and Research Awsari(khurd) Taluka-Ambegao, Dist-Pune.
Dr.V.M.Raut	Government Vidarbh Institute of Science and Humanities,Amravati

ABSTRACT

The thermal, electrochemical, photophysical, and electroluminescent properties of the new polyquinolines varied with the arylene linkage, including p-phenylene,4,4 -biphenylene,stilbene,5,5 -bithienylene,bis(thienyl)vinylene,and3,7-phenothiazinylene. The new conjugated polymers combined high glass transition temperature (110-254 °C) with quasireversible electrochemical reduction from which 2.72-3.00 eV electron affinities were estimated. The optical band gap varied from 2.19 to 2.86 eV whereas the photoluminescence emission maximum varied from blue-green (477 nm) to deep red (646 nm). Some of the new polymers with alternating donoracceptor architecture showed strong intramolecular charge transfer. Electroluminescence of moderate brightness (up to 209 cd/m2) was achieved with blue-green, green, yellow, orange, and deep red colors depending on the arylene linkage of the copolymer.

KEYWORDS :

Introduction

One area of great need is the development of new n-type conjugated polymers with good electron transport properties and a range of electron affinities or lowest unoccupied molecular orbital(LUMO) energy levels.[1,2] For use as electron transport materials in organic light-emitting diodes (OLEDs) a desirable range of the electron affinity (EA) is 2.7-3.4 eV, whereas much higher values (EA 3.84.5eV) are necessary for Ohmic contacts in photovoltaic cells and field effect transistors.[2,3d,4] Our group and others have previously shown that poly(phenylquinoline)s[6] and poly(alkylquinoline)s[7] are excellent electron transport materials for OLEDs due in part to their suitable EA values (2.6-3.0 eV) and rugged photochemical and thermal stability (Tg > 100 °C). Processability from formic acid allowed the poly(phenylquinoline)s to be successfully used in bilayer OLED devices with emissive p-type (hole transport) polymers such as poly(p-phenylenevinylene) (PPV)[6a,b] and poly(2-methoxy-5-(2 -ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV).[6c-f,7] Recent synthetic work has targeted organic-solvent-soluble polyquinolines in an effort to enhance processability and to permit more comprehensive characterization (e.g., solution spectroscopy on the neutral, nonprotonated species and gel permeation chromatography).

Experimental Section-
General Procedure for Polymerization.
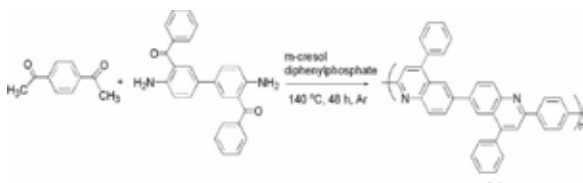
1 equiv of the diacetyl monomer, 1 equiv of 3,3 -dinonanoylbenzidine, 6.0 g of diphenyl phosphate, and 3g of m-cresol were added to a cylindrical reaction vessel. The reactor was purged with argon for 20 min. The mixture was mechanically stirred under static argon as the temperature was gradually raised to 140 °C over a period of 12 h. The polymerization mixture was stirred at this temperature for 72 h and then precipitated into 10% triethylamine/ethanol. The precipitate was collected by vacuum filtration and extracted on a Soxhlet apparatus for 72 h with 20% triethylamine/ethanol. The polymer was dissolved in CHCl3 and precipitated into ethanol, collected by vacuum filtration, and dried at 60 °C in a vacuum for 24 h.

Result and Discussion
Photophysical Properties

Absorption spectra of the six new polyquinolines in THF solution are shown in Figure 1a. The lowest energy absorption bands of most of the polymers are fromð-ð* transitions by virtue of their large molar extinction coefficients (_)(_max)(1.0-2.3)_104 M-1 cm-1). However, the lowest energy absorption bands of PBTOQ, PPZOQ, and PBTVOQ, which have a clear donor-acceptor architecture, can be interpreted in terms of intramolecular charge transfer (ICT).[19,20] The absorption maxima(ì max abs) of the polymers varies from 372 to 453 nm. The phenylene-, biphenylene-, and stilbene-linked polymers have the lowestì max abs values (372-398 nm). Theì max abs of PPZOQ, PBTOQ, and PBTVPQ show significant red shifts relative to these polymers because the donor acceptor architecture of the latter polymers facilitates large ICT. Donor-acceptor architectures in conjugated polymers is a well-known route to lowering the band gap of semiconducting polymers. [11,19,20] The thin film optical absorption spectra of the polymers are shown in Figure 1b. The solid-state absorption bands are red-shifted by 1-15 nm compared to their corresponding solution spectra. This phenomenon of increased electronic delocalization in thin films compared to solution is indicative of increased planarity of the polymer backbones in the solid state. The ìmax of the polymer thin films is in the range of 385-454 nm. The Eg opt values range from 2.19 to 2.86 eV, with PBTOQ (2.35 eV) and PBTVOQ (2.19 eV) having the lowest values. A comparison of the solid-state absorption spectra of the present poly (bis (4-alkyl quinoline))s to analogous poly(phenylquinoline)s shows a blue shift of 7-19 nm. This indicates that theð-orbitals of the phenyl side group have some electronic interaction with those of the backbone quinoline unit. The dilute solution (10-6 M) photoluminescence (PL) spectra of the polymers in THF are shown in Figure 2a.Five of the polymers have highly structured emission bands whereas the emission band of PPZOQ is structureless. The emission maximum varies from 413 nm for PPOQ and 538 nm for PPZOQ. The PL quantum yield (-f) of the polymers in dilute solution in THF was 11-24% (Table 1). The Stokes shift is between 33 and 49 nm for the polymers, except PPZOQ in which it is 124 nm. Previously, the analogous phenothiazylene linked poly(phenylquinoline) (PPZPQ)[19a] was not studied in solution in the neutral state. However, the solid-state emission of PPZPQ and that of a model compound were established to be due to intramolecular excitons with strong charge-transfer character. We believe that ICT also explains the large Stokes shift in the PL emission of PPZOQ. Although the PL quantum yields of these polymers (11-24%) are low, they are comparable to those of other soluble polyquinolines. [6b,7,10] The PL emission spectra of the polymer thin films are shown Figure 2b. All the PL emission spectra have broad and structureless line shapes, with emission maxima (ì max em) from 477 nm (PBOQ) to 646 nm(PBTVOQ). Thus, variation of the arylene linkage effectively tunes the PL emission color of the polymers. Five of the polymers showed an increased Stokes shift relative to that observed in solution. These features of the thin film PL emission spectra are indicative of aggregation effects and significant excimer formation.[21] However, PPZOQ thin films displayed approximately the same Stokes shift as in solution, indicating that the PL emission arises from an intramolecular chargetransfer excited state. A rough estimate of the solidstate fluorescence quantum efficiencies of these films with-

out an integrated sphere shows that they are low (1-8%), consistent with other polyquinolines. 6c,d,7,10

Electroluminescence and Electron Transport Properties.
We investigated the intrinsic electroluminescence (EL) of the new polyquinolines by using poly-(ethylenedioxythiophene)/poly(styrenesulfonic acid) (PEDOT) thin film on indium tin oxide (ITO) as the anode, poly(N-vinylcarbazole) (PVK) as the hole transport layer, the spin-coated polyquinoline as the emissive layer, and aluminum as the cathode: ITO/PEDOT/PVK/polyquinoline/Al. The film thicknesses of the emissive polyquinolines were_75 nm. Representative EL spectra of four of the polymers are shown in Figure 3a. Emission maxima (i max EL) varied from 513 to 656 nm (Table 1),indicating that we can effectively tune the emission color from blue-green to red by varying the arylene linkage.The EL maxima for PPOQ, PBOQ, and PSHQ are between 513 and 580 nm. The EL spectra for these polymers are considerably red-shifted 36-87 nm, relative to the PL spectra. The 551-656 nm EL maxima of PBTOQ, PBTVOQ, and PPZOQ are more consistent with the PL maxima. The turn-on voltage (electric field) of the diodes was 8.5-12V(_1.2_106V/cm). PPZOQ, which has the smallest barrier to hole injection (IP)5.17 eV), has the lowest turn-on voltage. The generally high turn-on voltages of these diodes are because of the large film thicknesses and the large barriers for charge injection.The brightness of the OLEDs was 69-209 cd/m2, and the external quantum efficiency (EQE) was 0.01-0.05% (Table 1). The device efficiency and brightness are in accord with the poor fluorescence quantum yields of thin films and the large barrier to hole injection into the n-type polymers. The OLED performance of the new polyquinolines is comparable to those of previous polyquinoline devices.6c,d,7,10,22 n-Type (electron transport) polymers that can be used in bilayer OLED architectures with organic-solvent soluble emissive polymers are relatively scarce, although some polypyridines, polyquinolines, and poly- quinoxalines that are soluble in formic acid have been explored.3a,6,7 Such an electron transport material (ETM) can increase device performance by reducing the barrier to electron injection, by blocking holes, and by moving the recombination zone away from the cathode. We have investigated the electron transport properties of the new polyquinolines by using MEH-PPV as the emissive polymer in LEDs of the type ITO/PEDOT/MEH-PPV/polyquinoline/Al. The film thickness of the polyquinolines as an electron transport layer in these diodes was in the range of 55-60 nm. These OLEDs showed EL spectra characteristic of MEH-PPV, having an emission peak at about 580 nm as exemplified in Figure 3b. The diodes showed no emission from the polyquinoline layer,
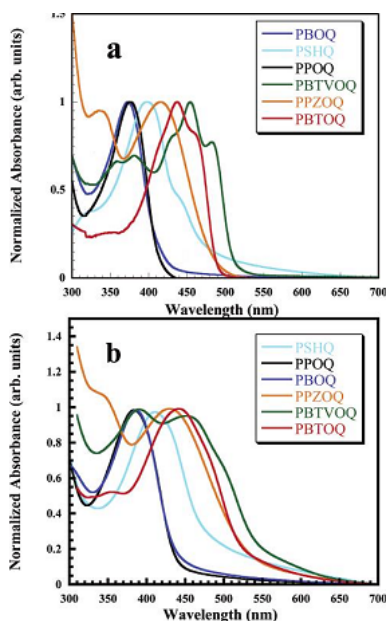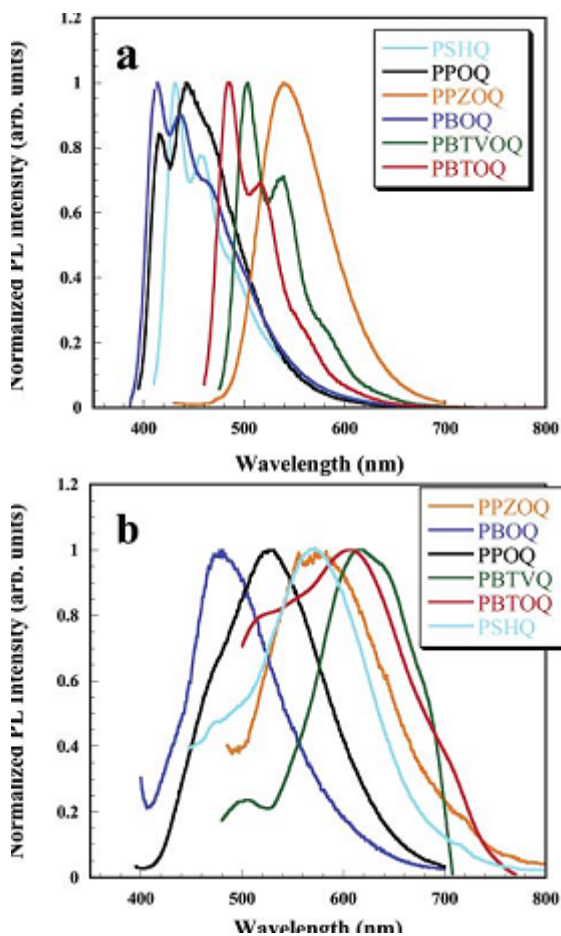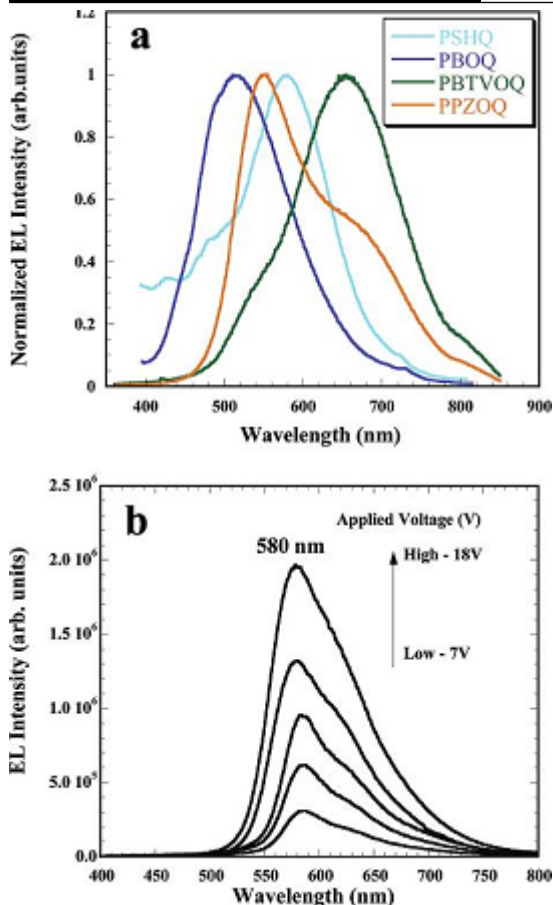

Figure 2. Photoluminescence (PL) spectra of new polyquinolines in dilute THF (10-6M) solutions (a) and as thin films (b). All polymers were excited at their respective absorption maximum.

indicating that recombination was occurring strictly in the MEH-PPV. The current-voltage and luminancevoltage characteristics of the MEH-PPV diodes using the new polyquinolines as electron transport materials are shown in Figure 8. The turn-on voltage (electric field) of these LEDs was 4.5-8.0V(_9_105V/cm).The best performance was found in diodes using PBTVOQ as the electron transport material, achieving a brightness of 740 cd/m2 and an external quantum efficiency of 0.12%. PSHQ based diodes had a similar brightness (659 cd/m2) and efficiency (0.11%) but a lower turn-on voltage of 4.5 V. This represents an increase in both brightness and efficiency over single-layer MEHPPV devices or single-layer polyquinoline diodes. Diodes using the other polyquinolines as ETMs had brightnesses of 451-557 cd/m2 and EL device efficiencies (EQEs) between 0.08 and 0.11%. It is reasonable to conclude that the performance of all the MEH-PPV diodes incorporating these polyquinolines as ETMs is in the same range. The performance of these diodes is equal to or higher than other recent work where polyquinolines were employed strictly as the electron transport layer with emissive MEH-PPV.6e,f However,these results are considerably lower than those based on polyquinolines incorporating a bis(phenylquinoline) and a regioregular dialkylbithiophene in the backbone.6c,d The molecular weights of those previous polyquinolines were significantly higher ((1.9-14.9)_104) than the present materials.6c,d The lower molecular weights of the present polyquinolines may account for their poorer performance as ETMs, compared to our previously reported materials, since the electron affinities of the two classes of polyquinolines are comparable.

Figure 1.Optical absorption spectra of new polyquinolines in dilute THF (10-6 M) solutions (a) and as thin films (b).

Figure 3. Electroluminescence (EL) spectra of selected polyquino-lines in ITO/PEDOT/PVK/polyquinoline/Al diodes (a) and for a ITO/PE-DOT/MEH-PPV/PPOQ/Al diode (b).

Table 3. Electroluminescent Device Properties of New Polyquinolines

Conclusions

The new polymers derived from this monomer contained bis(4-alky-lquinoline) in the main chain, facilitating solubility in organic solvents. The polymers had glass transitions of 110-254 °C and decomposed at above 400 °C, proving them to be thermally robust materials suitable for application in organic electronic devices. By varying the arylene linkage in poly(2,2 -arylene-6,6 -bis(4-alkylquinoline))s fromp-phe-nylene to bis(thienyl)vinylene, the optical band gap, redox properties, and electroluminescence color could be tuned over a wide range. The electron affinity or LUMO energy level of the polymers was in the range 2.72-3.00 eV, and blue-green, green,yellow, orange, and red electroluminescence colors were achieved with moderate bright-ness and efficiency. Enhanced electroluminescence efficiency and brightness were obtained from bilayer OLEDs based on MEH-PPV as the emitter and the new polyquinolines as the electron transport lay-er.The bis(4-alkylquinoline) platform demonstrated here allows the ready synthesis of diverse new soluble polyquinolines; it thus opens the door to further exploration of this n-type building block in new materials for organic electronics. New polymer structures incorporat-ing more exotic arylene linkages may allow the optimization of the materials for improved performance in optoelectronic devices.

Acknowledgement

REFERENCES   [1] [a] P.D. Sybert, W.H. Beever, J.K. Stille, Macromolecules 1981, 14, 493. [b] E.K. Zimmerman, J.K. Stille, Macromolecules 1985, 18, 321. [c] M.W. Pelter, J.K. Stille, Macromolecules 1990, 23, 2418. [2] [a] A.K. Agrawal, S.A. Jenekhe, Chem. Mater. 1992, 4, 95. [b] A.K. Agrawal, S.A. Jenekhe, Macromolecules 1993, 26, 895. [3] A.K. Agrawal, S.A. Jenekhe, Chem. Mater. 1996, 8, 579. [4] M.A. Abkowitz, M. Stolka, H. Antoniadis, A.K. Agrawal, S.A. Jenekhe, Solid State Commun. 1992, 83, 937. [5] A.K. Agrawal, S.A. Jenekhe, H. Vanherzeele, J.S. Meth, J. Phys. Chem. 1992, 96, 2837. [6] S.A. Jenekhe, X. Zhang, X.L. Chen, V.-E. Choong, Y. Gao, B.R. Hsieh, Chem. Mater. 1997, 9, 409. [7] D.M. Sutherlin, J.K. Stille, Macromolecules 1985, 18, 2669. [8] G.S. Skinner, J.A. Gladner, R.F. Heitmiller, J. Am. Chem. Soc. 1951, 73, 2230. [9] R.B. Davis, L.C. Pizzini, J. Org. Chem. 1960, 25, 1884. [10] S.A. Jenekhe, J.A. Osaheni, Science 1994, 265, 765. [11] J.A. Osaheni, S.A. Jenekhe, J. Am. Chem. Soc. 1995, 117, 7389. [12] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. MacKay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 1990, 347, 539. [13] N.C. Greenham, R.H. Friend, D.C.C. Bradley, Adv. Mater. 1994, 6, 491.