Plastic Electronics and Optoelectronics: Advances in Materials and Devices

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Introduction

Many advances have recently been made towards the development of plastic electronics based on the wide range of electronic, optoelectronic, and photonic properties of organic, oligomer, and conjugated polymer semiconductors [1-11]. As bulk thin films, conjugated polymers are being used in solid state devices including light emitting diodes for displays and lighting, photovoltaic cells, and thin film transistors [1,2]. In this lecture, I will describe recent work in our laboratory in these areas through several examples that illustrate our efforts in the molecular and supramolecular engineering of materials and devices for these applications [3-5,7,8a,10]. One of our central findings is that the supramolecular self-assembly and morphology of conjugated polymers and oligomers can have a dominant influence on their electronic and photonic properties and the performance of devices [10].

Results and discussion

We have developed new highly emissive multifunctional materials for next-generation, high performance and high durability OLEDs, including: (i) fluorene-acceptor copolymers for blue OLEDs [3], (ii) *n-type* emissive oligomers for blue OLEDs [4], (iii) donor-acceptor polyfluorene copolymers for white EL, and (iv) *bipolar* organic emitters for RGB OLEDs [5].

Achievement of stable *blue electroluminescence* (EL) with high efficiency, good color purity and long operational lifetimes at practical device brightnesses (> 100 cd/m^2) has been most challenging, in both polymer and small molecule OLEDs. We have investigated two series of polyfluorene copolymers containing different acceptor moieties (Chart 1) with the aim of improving the electron transport properties for use as emitters in blue OLEDs. The acceptor moieties used were 2,3-bis(*p*-phenylene)-quinoxaline and dibenzo[a,c]phenazine that were incorporated in various ratios in the polyfluorene backbone by Suzuki
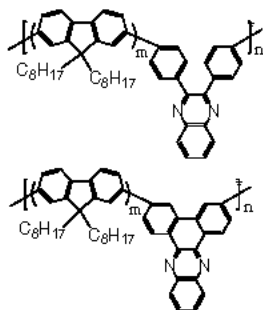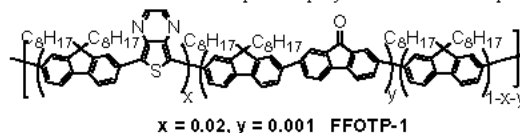

Chart 1. Structures of robust blue light-emitting polyfluorene copolymers.

coupling polymerization. Stable blue EL with external quantum efficiencies (EQEs) of 1% at brightnesses >100 cd/m^2 were obtained from diodes based on the QXF copolymers [3]. Better performance was achieved from the BPZF copolymers with EQEs of 2-4% at high brightnesses of >500 cd/m^2. We have also synthesized a new family of thermally robust, blue-emitting n-type oligoquinolines consisting of a 6,6'-bis(4-phenylquinoline) core and diverse aryl end groups [4]. Simple bilayer OLEDs based on 6,6'-bis(2-*p*-biphenyl)-4-phenylquinoline) (B2PPQ) as the blue emitter gave the best performance with a high brightness (19740 cd/m^2 at 8.0 V), high efficiency (7.12 cd/A and 6.56% EQE at 1175 cd/m^2) and excellent blue color purity with CIE coordinates of x=0.15, y=0.16 [4b]. These results represent the best efficiency of blue OLEDs from neat fluorescent organic emitters reported to date.

There is wide current interest in developing single white-light-emitting polymers for bright and efficient white EL from potentially simple, single-layer devices [6]. Towards this goal, we are investigating polyfluorene copolymers containing on-chain

thienopyrazine and fluorenone as the red and green emitting moieties, respectively (see Chart 2). Preliminary results indicate that good white CIE coordinates of (0.35, 0.28) can be obtained in the single-layer OLEDs based on such multicomponent polymers. Donor-acceptor (D-

x = 0.02, y = 0.001 FFOTP-1

Chart 2. Structure of thienopyrazine-containing polyfluorenes as potential candidates for white EL from a single polymer.

A) molecules capable of bipolar charge transport and efficient intramolecular charge transfer (ICT) fluorescence are also of wide current interest as emitters in OLEDs [5]. We have combined *phenothiazine* and *phenoxazine*, strong electron donors that have not been explored as building blocks in current OLED materials, with a variety of acceptors to develop a library of novel emissive D-A molecules. Very high brightness (> 40000 cd/m^2) and high efficiency
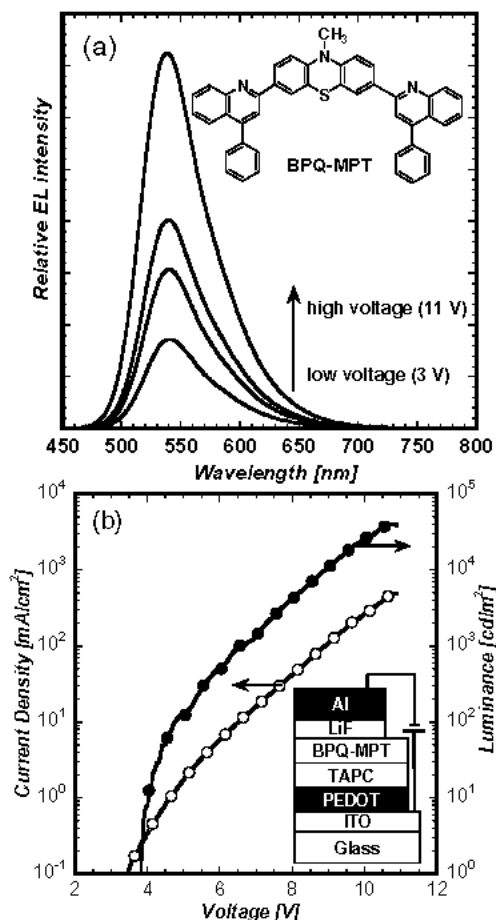

Figure 1. (a) EL spectra of a BPQ-MPT OLED. The inset shows the molecular structure of the D-A molecule. (b) Current density-voltage-luminance characteristics of the same device. The inset shows the device schematic.

(22 cd/A, 11 lm/W, 5.8% EQE at 1140 cd/m^2) green EL has been realized from OLEDs based on a phenothiazine-quinoline D-A molecule [5d], clearly demonstrating the potential of such D-A architectures in developing high-performance OLEDs (see Figure 1). Bright and efficient OLEDs with EL colors spanning the entire visible region (RGB) have been achieved from phenoxazine-based emissive D-A molecules containing different acceptors [5c].

The development of new solution-processable conjugated polymer semiconductors that have high charge carrier mobilities is of great importance for the advancement of organic electronic devices such as organic field-effect transistors (OFETs), photovoltaic cells,

and organic light-emitting diodes (OLEDs) [1,2]. One of the key challenges is to develop new building blocks for the design of polymer semiconductors for OFETs and other organic electronic devices. We have explored the tricyclic phenoxazine ring as a new building block for the construction of organic and polymer semiconductors for organic electronics [5c,7]. The ionization potential of phenoxazine is 0.7 eV lower compared to that of carbazole ring which has been widely used in organic electronics and this means that its radical cations (or holes) are more stable. We have recently synthesized and investigated several phenoxazine-based π-conjugated polymers [7], including the phenoxazine-thiophene and phenoxazine-fluorene copolymers (Chart 3). These polymers have high glass transition temperatures (112-230 °C) and highly reversible electrochemical oxidation and low ionization potentials (4.8-4.9 eV).

R = heptyl, decyl, dodecyl
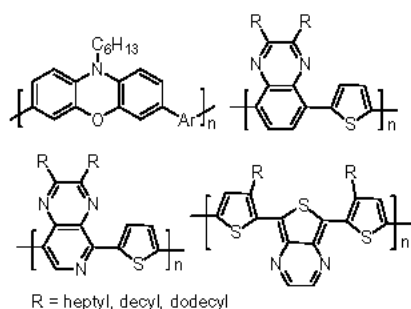
Chart 3. Molecular structures of phenoxazine-based and donor-acceptor copolymers.

Thin-film transistors based on polyphenoxazine and its copolymers showed typical p-channel output characteristics with good drain current modulation and well-defined linear and saturation regions when operated in accumulation mode. A maximum hole mobility of 6×10^{-4} cm^2/Vs and on/off ratio of 10^4 was measured in thin film transistors based on the alternating phenoxazine-thiophene copolymer [7]. The low ionization potential (4.8-4.9 eV) of the phenoxazine-containing copolymers facilitates ready injection of holes from gold and other high work function electrodes in OFETs. Our results thus demonstrate that phenoxazine is a promising new building block for the design of p-type semiconductors for OFETs and other device applications.

Conjugated polymers with donor-acceptor (D-A) architectures are of growing interest for ambipolar OFETs [8], photovoltaic cells [9], and other electronic devices since their electronic and optoelectronic properties can be tuned efficiently by intramolecular charge transfer between the donor (p-type) and acceptor (n-type) building blocks [5a]. Organic semiconductors that combine high electron affinity and low ionization potential with broad absorption bands extending into the near infrared, small band gaps, and high charge carrier mobilities, of great interest for photovoltaic cells, can be realized in D-A copolymers incorporating strong donors and acceptors. Achievement of ambipolar charge transport with high hole and electron mobilities, which is of importance for the development of complementary integrated circuits technology and has been very challenging to realize in polymer semiconductors, could in principle also be facilitated by D-A copolymers with strong donors and acceptors.

We have recently synthesized several solution processable D-A copolymers incoporating quinoxaline, pyrido[3,4-b]pyrazine or thienopyrazine units as the acceptor and thiophene or bithiophene units as the donor (Chart 3). Their electronic, optical, and charge transport properties were investigated. The thin film optical absorption spectra showed broad absorption bands with lowest energy absorption maxima of 630-660 nm for quinoxaline or pyridopyrazine-thiophene copolymers and 780 nm for thienopyrazine-thiophene copolymer. The optical band gaps were estimated to be 1.7-1.8 eV for quinoxaline or pyridopyrazine-thiophene copolymers and 1.1 eV for thienopyrazine-thiophene copolymer. This clearly shows that the harvesting of the solar spectrum in the near infrared spectral range (700-1200 nm) was greatly improved by incorporating strong acceptor thienopyrazine units into D-A copolymers.

All the OFETs based on the D-A copolymers showed typical p-channel output characteristics with good source-drain-current modulation and well-defined linear and saturation regions when operated in accumulation mode [8a]. A saturation hole mobility of up

to $\sim 8 \times 10^{-3}$ cm$^2 \cdot$V$^{-1} \cdot$s^{-1} and on/off current ratios of $5 \times 10^5 - 5 \times 10^6$ were achieved in the D-A copolymers. Ambipolar OFETs have also been achieved in D/A polymer blends [11].

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