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, oligomers, and conjugated polymer semiconductors [1-11]. As bulk thin films, conjugated polymers are being used in solid state devices including light emitting diodes for display 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: (a) fluorine-acceptor copolymers for blue OLEDs [3], (b) p-type emissive oligomers for blue OLEDs [4], (c) donor-acceptor polyfluorene copolymers for white EL, and (d) bipolar organic emitters for RGB OLEDs [5].

Achievements of stable blue electroluminescence (EL) with high efficiency, good color purity and long operational lifetimes at practical device brightnesses (>100 cd/m²) 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 2,5-bis(3-phenylquinoxaline) and dibenz[a]acridine that were incorporated in various ratios in the polyfluorene backbone by Suzuki coupling polymerization. Stable blue EL with external quantum efficiencies (EQE) of 8% at brightnesses >100 cd/m² were obtained from devices based on the QP copolymers [3]. Better performance was achieved from the BQF copolymers based on BQF of 2-4% at high brightnesses >800 cd/m² [4]. We also synthesized a new family of thermally robust, blue-emitting n-type oligomers consisting of a 6,6’-bis(4-phenylquinoline) core and diverse aryl end groups [4]. Single layer OLEDs based on 6,6’-bis(2-ethylhexyl)-4,4’-dimethylquinoline (E272Q) as the blue emitter gave the best performance with a high brightness (1974 cd/m² at 50 V), high efficiency (7.12 cd/A and 6.56% EQE at 1775 cd/m²) and excellent blue color purity with CIE coordinates of x=0.14, y=0.15 [4]. These results represent the best efficiency of blue OLEDs from near 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 co-chain thienopyrazine and fluoranthene 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-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 phenazine and phenanthrene, 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/m²) and high efficiency

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

![Chart 1](image)

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

![Chart 2](image)

Figure 1. (a) EL spectra of a BQF-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 1740 cd/m²) green EL has been realized from OLEDs based on a phenazine-quinoline D-A molecule [5] 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 fluorescein-based emissive D-A molecules containing different acceptors [5].

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 electronic devices. We have explored the triarylimidazole ring as a new building block for the construction of organic and polymer semiconductors for organic electronics [5,6]. The ionization potential of phenazine is 0.7 eV lower compared to that of carbazole, which has been widely used in organic electronics and thus means that its radical cations (or holes) are more stable. We have recently synthesized and investigated several phenazine-based n-conjugated polymers [7], including the phenazine-thiophene and phenazine-fluorene copolymers (Chart 3). These polymers have high glass transition temperatures (112-230 °C) and highly reversible electroluminescent emission and low ionization potentials (4.3-4.9 eV).

Thin-film transistors based on phenazine-based 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 cm²/V·s and on/off current ratio of 10⁵ was measured in thin film transistors based on the alternating phenazine-thiophene copolymer [7]. The low ionization potential (4.3-4.9 eV) of the phenazine-containing copolymers facilitates direct injection of holes from gold and other high work-function electrodes in OFETs. Our results thus demonstrate that phenazine is a promising new building block for the design of p-type semiconductors for OFETs and other devices 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 intercalation 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 high 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 donor and acceptor chromophores. A high-achieving ambipolar charge transport with high hole and electron mobilities, which is of importance for the development of complementary integrated circuit 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 incorporating quinoline, pyridine-thiophene or thiophene-thiophene 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 quinoline or pyridine-thiophene copolymers and 780 nm for thiophene-thiophene copolymers. The optical band gaps were estimated to be 1.7-1.9 eV for quinoline or pyridine-thiophene copolymers and 1.1 eV for thiophene-thiophene copolymers. 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 chromophores 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 8 × 10⁻⁴ cm²/V·s¹ and on/off current ratios of 6.10⁵ – 10⁶ were achieved in the D-A copolymers. Ambipolar OFETs have also been achieved in D-A polymer blends [11].

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