

Glass-Forming Organic Semiconductors for Optoelectronics

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Organic electronics and optoelectronics are newly emerging fields of science and technology that cover chemistry, physics, and materials science. Electronic and optoelectronic devices using organic materials are attractive because of the materials characteristics, potentially low cost, and capability of large-area, flexible device fabrication. Such devices as OLEDs, OPVs, and OFETs involve charge transport as a main process in their operation processes, and therefore, require high-performance charge-transporting materials. This review article focuses on charge-transporting materials for use in OLEDs, OPVs, and OFETs. We have tried to arrange the charge-transporting materials in order by classifying them on the basis of their molecular structures. Molecular design concepts for charge-transporting materials and their charge-transport properties are discussed.

Keywords: charge-transporting, molecular glasses, polymers.

1. INTRODUCTION

Optoelectronic and electronic devices, such as organic light-emitting diodes (OLEDs), organic photovoltaic devices (OPVs), organic field-effect transistors (OFETs), organic electrophotographic photoreceptors, electrochromic devices have received a great deal of attention from the standpoint of present and potential technological applications as well as fundamental science [1–10]. Organic electronic and optoelectronic devices in general have the advantages of being light weight, rugged and flexible, potentially low cost, and ready fabrication for large-area applications, leading to many possible new applications.

Among organic materials used in optoelectronic devices important role belongs to organic semiconductors, which are responsible for charge carrier transport and often for charge generation or injection. When organic materials are used in optoelectronic devices, they are normally in the form of thin films. Organic thin films can be prepared by various techniques, e.g. solvent cast, spin coating, vacuum deposition, electrochemical deposition, Langmuir-Blodgett and monolayer self-assembly techniques. Both ordered and disordered (amorphous) films can be generated, depending on the technique and condition of thin film fabrication.

Charge transporting materials are classified into p-type (hole-transporting), n-type (electron-transporting) and bipolar materials depending upon the kind of charge carriers transported. Hole or electron transport occurs by the transfer of charges from states associated with the donor and acceptor functionalities, respectively. This process can be described as a one electron oxidation-reduction process. The charge transport in condensed organic systems, in general, depends on both the molecules themselves and the way they are assembled in the condensed phase. Furthermore, different technical applications may have different requirements on materials, such as thermal stability, electrochemical stability, morphological stability, charge carrier mobility and etc.

In this article the most relevant structures, properties of organic low-molar-mass and polymeric organic semiconductors will be reviewed. The materials synthesized in the laboratories of the authors will be emphasized.

2. APPLICATIONS

Organic light-emitting diodes. These devices are also often named as electroluminescent (EL) devices. They have in recent years received a great deal of attention for their applications in efficient, large-area and full-color flat-panel displays [11, 12]. Following the reports on organic EL devices using single crystals of anthracene [11, 12], the later pioneering works on organic EL devices using low molecular weight organic materials and conjugated polymers have triggered extensive research and development [1, 13].

The typical structure of organic EL devices (Fig. 1) consists of single or multiple layers of organic thin films sandwiched normally between the transparent indium-tin-oxide (ITO) anode on glass and vacuum-deposited metals cathodes. The operation of OLEDs involves injection of holes and electrons from the ITO anode and the metal cathode, respectively, transport of injected charge carriers, recombination of holes and electrons in the emission layer to generate an electronically excited-state molecules, giving luminescence. In order to achieve high performance in OLEDs, it is usually necessary to achieve charge balance. Generally, layered devices consisting of charge-transport and emitting layers can more readily achieve charge balance than single-layer devices using charge-transporting and emitting material alone.

Generally, materials for use in OLEDs should meet the following requirements [4, 11, 12, 14, 15]: (a) to possess suitable energy levels (ionization potentials, electron affinity) for carrier injection from electrodes or for carrier confinement at organic/organic interfaces, (b) to be capable of forming uniform films, (c) to be morphologically, thermally and electrochemically stable. In addition to these general requirements, materials should meet further specialized needs depending upon the roles that they play in

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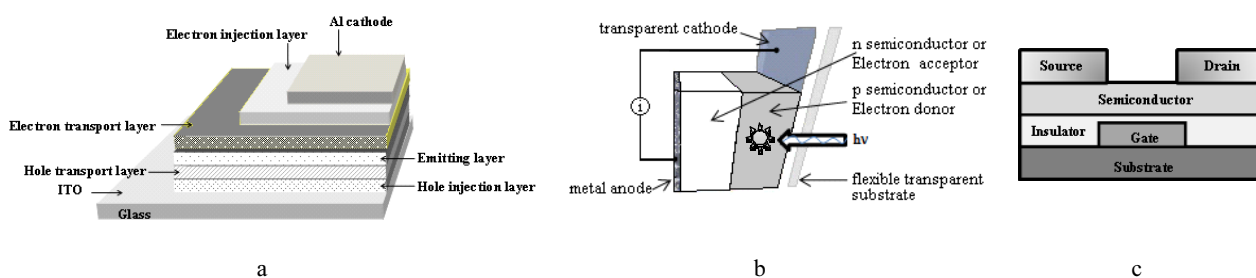


Fig. 1. Schematic representation of: (a) multilayer OLED, (b) OPV device, (c) organic semiconducting TFT with top contacts

devices, for example, hole transport, electron transport, charge blocking, and light emission.

Some of the hole-transporting compounds like star-shaped derivatives have been successfully used in multilayer OLEDs [4]. Electron-transporting molecular glasses like Alq₃, oxadiazole [16], and phenylquinoxaline [17] derivatives enable to balance charge transport in OLEDs and thus to improve their characteristics.

Organic photovoltaic devices. Another challenging field of application of organic charge-transport materials is the conversion of solar energy into electric energy. It is based on the photovoltaic effect by which electrons and holes are produced, as the result of photoexcited electron transfer between donor and acceptor molecules, and collected at electrodes. These semiconductor devices are usually called photovoltaic devices or solar cells. Organic solar cells have been reviewed [18, 19].

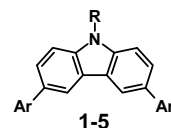
Commercially realistic efficiencies have been achieved in solar cells based on dye-sensitized mesomorphous films of TiO₂ [20]. The device contains a 10 μm-thick, optically transparent film of titanium dioxide particles of a few nanometers in size, coated with a monolayer of a charge-transfer ruthenium complex to sensitize the film for light harvesting. An overall light-to-electric energy conversion efficiency of 10% was achieved with such films when used in conjunction with liquid electrolytes such as LiI/I₂ in acetonitrile [21]. Practical advantages may be gained if the liquid electrolytes are replaced with by solid-state charge-transport materials. Amorphous hole-transport materials have been successfully used for this purpose [22, 23].

Organic field-effect transistors are expected to be promising devices for large-area, low cost, and flexible electronics for applications in displays, sensors, and memories [24]. Three fundamental device components are the contacts (source, drain, and gate), the semiconductor, and the dielectric layers, typically arranged according to the device configuration shown in Fig. 1. Since the reports on OFETs using polythiophene [25] and phthalocyanine [26] appeared, there have been extensive studies on OFETs using oligothiophenes and their analogues [27, 28] and other numerous kinds of organic semiconductors, such as oligofluorenes [29], fullerenes [30–32], hydrazones [33, 34].

3. CHARGE TRANSPORTING MOLECULAR GLASSES

As molecular glasses or amorphous molecular materials are defined low-molar mass compounds, which can exist in a glassy state at ambient and higher temperatures and form solid amorphous films on substrates [35].

Compounds with a central carbazole core. Carbazole moiety with charge transporting function has been widely used in the molecular design of new types of organic semiconductors. The nitrogen atom of carbazole can be easily substituted with a wide variety of functional groups to help with the solubility of the materials and to tune their thermal, optical and electrical properties. On the other hand, carbazole core can be easily substituted with the arylamino groups at its 3- and 6- positions. 3,6-di(arylamino)-9-alkyl(aryl)carbazoles (**1–5**) were prepared via Ullmann coupling of 3,6-diiodo-9-alkyl(aryl)carbazole with an excess of secondary amine i.e. diphenylamine, 9*H*-carbazole or 10*H*-phenothiazine, respectively [36–41].



	R	Ar
1 a	C ₂ H ₅	
1 b	C ₈ H ₁₇	
1 c		
1 d		
2	C ₄ H ₉	
3	C ₆ H ₁₃	
4 a	CH ₂ CH(C ₂ H ₅)C ₄ H ₉	
4 b	C ₈ H ₁₇	
4 c	C ₁₀ H ₂₁	
4 d		
5	C ₆ H ₁₃	

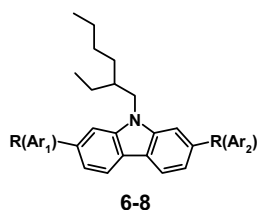
The thermal properties of the 3,6-di(arylamino)-substituted carbazoles were dependent on the substituents. 3,6-Di(N-diphenylamino)-9-alkyl(phenyl)carbazoles **1–3** were obtained as crystalline materials but they readily formed glasses when their melted samples were cooled. The glass transition temperature (*T_g*) and the thermal stability of the resulting materials greatly depended on the substituents at 9 position of carbazole core. The presence of bulky phenyl groups provided a more rigid structure **1 c, d** and resulted in an increase of *T_g* with respect to ethyl- or octyl-substituted derivatives **1 a** and **1 b** [36–38]. Carbazolyl- or phenothiazinyl-containing derivatives (**4** and **5**) demonstrated high *T_g*, however their amorphous films, except **4 c**, were morphologically unstable [39–41]. Carbazole derivatives **1–5** exhibited ionization potentials (*I_p*) ranging from 5.3 eV to 5.8 eV. The values of *I_p* were affected by the nature of substituents at 3 and 6 positions of carbazole ring and decreased in the order diphenylamino

(1 c) < phenothiazinyl (5) < carbazolyl (4 a) [38, 40, 41]. Hole drift mobilities in the range of $(10^{-3} - 10^{-6}) \text{ cm}^2/\text{V}\cdot\text{s}$ were observed for amorphous films of the materials. Carbazolyl-containing derivatives 4 a and 4 c were demonstrated to be promising host materials for multilayer OLEDs [39], which achieved maximum brightness of nearly 60000 cd/m^2 (at 14 V).

Compounds containing 2,7-substituted carbazolyl unit has recently attracted much attention [42]. The synthesis of these compounds is much more difficult, compared to that of 3,6-substituted carbazole derivatives, since 3- and 6-positions of the carbazole moiety are activated by the nitrogen atom. All kinds of electrophilic substitution reactions can take place in these positions. 2- and 2,7-substituted carbazole derivatives 6, 7 and 8 incorporating carbazolyl groups at 2 and 7 positions were prepared via palladium catalyzed C–N or C–C bond formation [43].

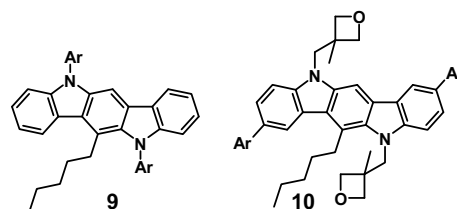
2,7-Substituted carbazole compounds 6–8 formed amorphous films. These compounds were crystallized from solution, but could be converted to glasses upon cooling of the melts. 2,7-Di(9-carbazolyl)-9-(2-ethylhexyl)carbazole 7 showed higher T_g than mono substituted analogue 6 a [43].

Electron photoemission spectra revealed I_p of ca. 5.8 eV in the amorphous layers of the 2,7-substituted carbazole compounds 6–8. Hole mobilities were measured in the films of the materials by time-of-flight (TOF) transient photocurrent technique in vacuum at room temperature, and exceeded $10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$. The relatively high electron mobilities were observed for 2,7-disubstituted carbazole compound 7 (ca. $10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$) [43]. The hole and electron mobilities in the amorphous films of the 2,7-disubstituted carbazole compound 7 are by one to two orders of magnitude higher than those of the 3,6-disubstituted congener 4 a [43].



	R(Ar ₁)	R(Ar ₂)
6	H	
7		
8	H	

Compounds with a central indolo[3,2-*b*]carbazole core. The indolo[3,2-*b*]carbazole-based compounds 9 a–c were synthesized via modified Ullmann coupling reaction of 6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole with an excess of arylhalogenide [44]. Compound 10 a was obtained by Suzuki-Miyaura coupling of 6-pentylindolo[3,2-*b*]carbazole derivative with an excess of phenylboronic acid 1,3-propanediol ester [45]. Compounds 10 b, c were prepared by Buchwald-Hartwig procedure with diphenylamine or 10*H*-phenothiazine, respectively [45].



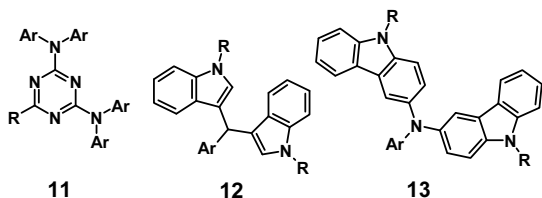
	Ar		Ar
9 a		10 a	
9 b		10 b	
9 c		10 c	

5,11- and 2,8-disubstituted indolo[3,2-*b*]carbazole compounds 9 and 10 formed amorphous films. All these compounds, except 9 b, were crystallized from solution, but could be converted to a stable glass upon cooling of the melt [44,45]. Carbazolyl-containing compound 9 b was amorphous in nature and exhibited moderate T_g . 2,8-disubstituted indolo[3,2-*b*]carbazole compounds 10 showed considerably higher T_g than 5,11-disubstituted compounds 9. 5,11- and 2,8-disubstituted indolo[3,2-*b*]carbazole derivatives 9 and 10 exhibited rather close values of I_p ranging from 5.20 eV to 5.48 eV. The best charge transport properties were demonstrated by fluorenyl-containing compound 9 c. Hole drift mobility exceeding $10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ was recorded at an electric field of $3.6 \times 10^5 \text{ V/cm}$ for the amorphous layer of the material by xerographic TOF technique. Cross-linkable materials with 2,8-disubstituted indolo[3,2-*b*]carbazole core (10 a–c) were used as hole-transporting materials in bilayer OLEDs with 8-hydroxyquinoline (Alq_3) as an emitter [45]. The devices with phenyl substituted indolo[3,2-*b*]carbazole 10 a exhibited turn-on voltage: ~5 V; maximum luminescence efficiency: 3.64 cd/A; maximum brightness: approx. 5700 cd/m^2 . Cross-linked networks of compounds 10 a–c were also tested as hole transporting structures in multilayer OLEDs with green light emitting polymer [45]. The device containing cross-linked layer of phenyl substituted indolo[3,2-*b*]carbazole 10 a demonstrated maximum photometric efficiency of 2.8 cd/A and maximum brightness of 7790 cd/m^2 .

Star-shaped compounds. 1,3,5-Triazine-based star-shaped derivatives 11 were synthesized via Ullmann coupling reaction of 2,4-diamino-6-phenyl-1,3,5-triazine with an excess of arylhalogenide [46]. Indole-based compounds 12 were synthesized by the tandem addition-elimination-(Michael) addition reaction from 1*H*-indole and formyl derivative in the presence of concentrated hydrochloric acid [47, 48]. Di(9-alkylcarbazol-3-yl)arylamines 13 were prepared via Ullmann coupling reaction of 3-iodo-9-alkylcarbazole with the primary amine [49].

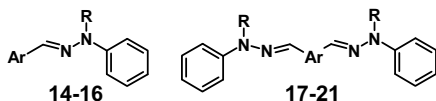
Compounds 11–13 formed glasses with T_g in the range of $(39 - 147)^\circ\text{C}$. Star-shaped compounds 11–13 exhibited very different I_p ranging from 4.9 eV to 5.83 eV [46–49]. The lowest I_p values were observed for triarylamines 13 having the bulky carbazolyl species. Solid solutions of 11 and 13 in bisphenol Z polycarbonate (PC-Z, 50 %) demonstrated hole drift mobility values

reaching $10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ at high electric fields. Indole-based star-shaped compounds **12** in dilute solutions exhibited relatively high triplet energies (2.97 eV–2.99 eV), which were higher than those reported for the common triplet blue emitters used in electrophosphorescent devices iridium(III)bis[(4,6-difluorophenyl)pyridinato- N,C^2] (Firpic) 2.62 eV [50].



	R	Ar		R	Ar
11 a			12 d	C_2H_5	
			13 a		
11 b			13 b	$\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	
12 a	C_2H_5		13 c		
12 b	C_4H_9				
12 c					

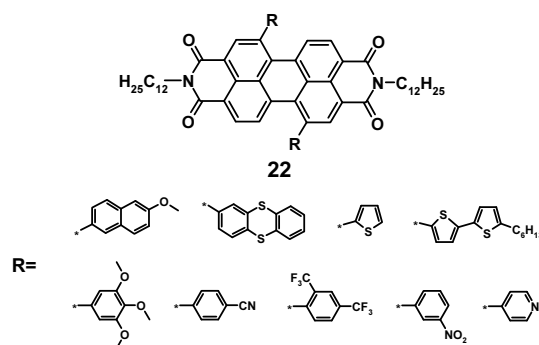
Arylhydrazones. Arylaldehyde and arylketone hydrazones constitute a big family of hole-transporting amorphous molecular materials [51]. The synthetic route to charge-transporting hydrazones usually includes formulation of an aromatic or heteroaromatic compound followed by condensation of the obtained aldehyde with mono or disubstituted hydrazine. The structures of hydrazones, in which arylhydrazone moieties are attached to the central carbazole, bicarbazole, triphenylamine, terthiophene, thiophene or 3,4-ethylenedioxythiophene core are shown below [52–59].



	R	Ar
14 a, 17 a		
14 b, 17 b	CH_3	
18 a		
18 b	CH_3	
19 a		
19 b	CH_3	
20 a		
20 b	CH_3	
15 b	CH_3	
16 a, 21 a		
16 b, 21 b	CH_3	

All these hydrazones were found to form molecular glasses. Monohydrazones **14–16** showed lower T_g than the corresponding dihydrazones **17–21**. The values of I_p of these materials were depended upon chromophore used and ranged from 4.99 eV to 5.60 eV. The lowest I_p values were observed for triphenylamine and 3,4-ethylenedioxythiophene-based dihydrazones **19** and **21** [52–59]. Hole drift mobilities of most of these hydrazones, doped in PC-Z reached (10^{-5} – 10^{-4}) $\text{cm}^2/\text{V}\cdot\text{s}$ at an electric field of 10^6 V/cm . Dihydrazones **17, 21** showed better charge transport properties than the corresponding monohydrazones **14, 16** [52, 53, 56, 59]. Terthiophene-based dihydrazone **20 a** has been applied as hole transport material for the solid state dye sensitized solar cell [58]. The results obtained confirm the feasibility to use hydrazone based molecular glasses for the elaboration of solid state dye-sensitized solar cells.

Aromatic imides are promising n-type materials. Naphthalenetetracarboxylic diimide, perylenetetracarboxylic diimide, pyromellitic diimide, and others aromatic imides are used as n-channel conductors in OFETs [60]. Perylenediimide derivatives are widely investigated organic materials with important applications in optoelectronics. Perylenediimide derivatives **22** were synthesized via Suzuki coupling reaction of dibromoperylene diimide with an excess of the corresponding monoboronic acid [61, 62].



The perylene derivatives were found to be thermally stable and capable of forming molecular glasses with the glass transition temperatures ranging from 50 °C to 102 °C. The cyclic voltammetry studies showed the presence of electron donating aryl units significantly lower the band gap [61]. Some of perylenediimide derivatives showed high luminescence quantum yield in solution (0.44–0.73) [62]. The xerographic TOF method revealed the electron mobility of some perylene derivatives could be achieved up to $10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ at 10^6 V/cm under ambient conditions [61].

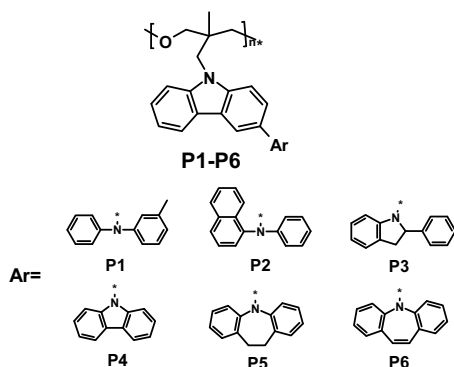
4. CHARGE-TRANSPORTING POLYMERS

Several polymer types and classes are known to exhibit charge-transporting properties. The known charge transporting polymers are prepared by almost all common methods like free-radical, cationic, anionic, coordination, and ring-opening polymerization, step-growth polymerization (polycondensation and polyaddition), and polymeranalogous reactions. The only common requirement for all charge-transporting materials is that they have to be of extreme purity. From the structural point

of view the polymers described in this review can be divided into two groups:

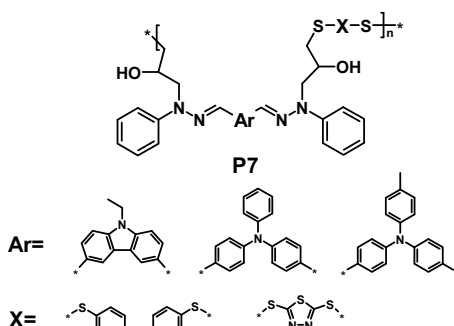
- Polymers with pendant or main chain active groups;
- Polymers with π -conjugated main chain.

Polymers with pendant or main chain active groups. Poly(*N*-vinylcarbazole) was the first to be recognized as a classical hole-transporting material as well as good photoconductor and was extensively exploited in xerographic application [5]. Later carbazolyl-containing polyethers were widely synthesized and studied [63, 64]. The advantage of carbazolyl-containing polyethers against poly(*N*-vinylcarbazole) were their better film-forming properties and the absence of excimer forming sites. Polymers with pendant 3-arylcarbazol-9-yl groups **P1**–**P6** were synthesized from oxetanyl-functionalized monomers by cationic polymerization [65–67].



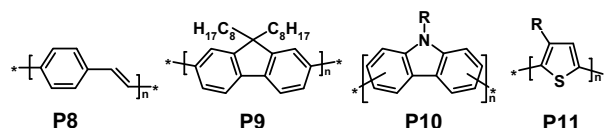
Polymers **P1**–**P6** exhibited T_g ranging from 162 °C to 203 °C. The values of I_p were affected by the nature of substituents at 3 position of carbazole ring. The lowest I_p values were observed for polymers **P5** and **P6** containing dibenzazepine substituted carbazolyl fragment, and reached 5.2 eV. Polymers **P1** and **P2** were studied as hole-transporting materials in bilayer OLEDs with Alq₃ as an emitter. The device with polymer **P2** exhibited the turn-on voltage of ca. 3 V, maximum photometric efficiency of 4.1 cd/A, maximum brightness of 22,900 cd/m². Polymer **P3** was tested as host material in phosphorescent OLEDs with different concentrations of iridium(III)[bis(4,6-difluorophenyl)-pyridinato-N,C2']picolinate (Firpic) as the guest. The device exhibited brightness of 280 cd/m², and a maximum power efficiency of 0.66 lm/W.

Hole-transporting polymers **P7** containing hydrazone moieties in the main chain were synthesized by polyaddition of diepoxy compounds with 4,4'-thiobisbenzenethiol or 2,5-dimercapto-1,3,4-thiadiazole [68, 69].



Hole drift mobilities in amorphous films of these polymers exceed 10^{−4} cm²/V·s at an electric field of 10⁶ V/cm. This is rather high mobility as for amorphous polymeric materials. Hole mobilities in polymers containing triphenylamino moieties is by ca. one order of magnitude higher than in polymers containing carbazolyl group.

Polymers with π -conjugated main chain. Poly(phenylenevinylene) (**P8**) was the first π -conjugated polymer in which the phenomenon of electroluminescence was demonstrated and from which OLEDs were fabricated [11], but polyfluorene derivatives were quickly investigated in electrooptical devices by Ohmori et al. [70].



The most widely studied among the polyfluorenes is poly(9,9'-dioctylfluorene) (**P9**), which was prepared by Suzuki coupling using bis-boronates [71]. This polymer forms a well defined thermotropic liquid crystalline state that can be aligned on rubbed substrates and can be either quenched into a glass or crystallised [72]. **P9** exhibits relatively high hole mobility, which is necessary, since in order to ensure an acceptable power efficiency high brightness of electroluminescent devices should be reached at low bias voltages. The as-spin coated ("isotropic") polymer film shows hole mobility of 3 × 10^{−4} cm²/V·s [73].

Poly(3,6-carbazole)s (**P10**) were used as blue-light emitters. Their rigid structure, hole-transporting ability and good film-forming properties made them potential candidates as blue-light emitters in OLEDs. This was confirmed with the achievement of the first OLEDs based on 3,6-carbazoles [74]. Poly(2,7-carbazole)s are a relatively newly discovered class of conjugated polymers. These polymers emit blue light under UV illumination, making them attractive for the development of blue light OLEDs [75–77].

Polythiophenes as well as poly(phenylenevinylene) are among the most investigated conjugated polymers. Their synthesis, properties and applications are described in detail in the book [78]. Poly(3-alkylthiophenes) (**P11**) have been found to show excellent charge-transporting properties [79, 80]. This fact as well as their processibility and stability render them attractive as active elements in electronic devices. Poly(3-alkylthiophenes) are used as p-channel conductors in OFETs [81], and p-type materials in OPV devices [82] with highest performance achieved to-date.

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