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Macromolecular systems with the p-type conductivity*

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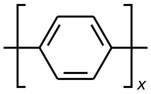
General concepts of organic (polymeric) electronics are given, a relationship between chemical structure of semiconducting macromolecular systems and their electronic properties is considered, main approaches to the control of these properties are listed. A relationship between dimensionality of the systems considered (one- , two-, and three-dimensional) and a possibility to control their molecular organization, as well as their practical use are illustrated. Typical representatives of both the linear and branched (two- and three-dimensional) macromolecules, approaches to the synthesis of such macromolecules, their optical and electrical properties, as well as prospective fields of application, are considered.

Key words: organic electronics, photonics, p-type semiconductivity, π-conjugated polymers.

Introduction

In the last years, a vast amount of studies were devoted to organic macromolecular systems possessing properties of (semi)conductors.[1—5] Such systems are a potential alternative to inorganic semiconductors in the production of cheap flexible optoelectronic devices, such as organic thin-film transistors (OTFT),[6—11] light-emitting diodes (OLED),[2,3] photovoltaic cells (OPV cells),[4] lasers, sensors, *etc*. As it is known, electronic devices based on inorganic conductors (metals) and semiconductors (for example, silicon) are produced by technologically complex methods of engraving or lithography including high-temperature steps of treatment, that sets considerable limits on such devices cost lower borderline. At the same time, semiconducting and conducting organic macromolecular systems combine advantages of plastics (such as low weight, transparency, and flexibility of devices obtained from them) with the simplicity of their preparation, for example, by obtaining thin films from solutions by a spin-coating method, jet or offset printing.

The first conducting macromolecular systems have been obtained by A. G. MacDiarmid, H. Shirakawa, and A. J. Heeger, for this works the authors were awarded a Nobel prize in 2000.[12—14] It turned out that π-conjugated polymers such as polyacetylenes, poly(*p*-phenylenes) (**1**), poly(phenylenevinylenes) (**2**), poly(pyrroles) (**3**), poly(thiophenes) (**4**), poly(furans) (**5**), *etc*. can possess conducting properties upon their doping (a dosed change in amount of electrons in the π-system of such polymeric chains). The latter can usually be accomplished by addition or removal of a certain amount of electrons by chemical or electrochemical means (redox doping), which leads to the formation of a delocalized π-system and, as a result, to considerable changes in electrical, magnetic, optical, and structural properties of such polymers, in particular, to the increase in electrical conductivity by several orders of magnitude.



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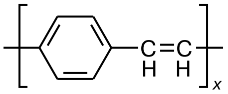

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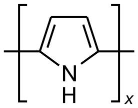

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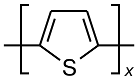

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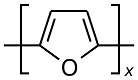

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In addition to the redox way, doping can also be accomplished by irradiation, "charge injection", or nonoxidative way. Materials with both the electron (n-type) and the hole (p-type) conductivity can be obtained by doping. In this case, such materials without doping, as a rule, possess semiconductor properties with the same type of base charge carriers as it is shown below in Section 1.

At present, the main challenge for researchers working in the field of organic electronics consists in development of the most simple methods for obtaining (semi)conducting polymers, stable under environmental conditions and possessing good semiconductor, luminescent, photovoltaic, and other properties. For many devices of organic electronics, a combination of good solubility of the material, ability to form films, high crystallinity, and narrow

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* Dedicated to Academician of the Russian Academy of Sciences I. L. Eremenko on occasion of his 60th birthday.

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enough band gap is a necessary condition. In addition, for obtaining high technical characteristics of devices on their basis a special attention should be devoted to a possibility to control morphology of the thin films from such materials on the nano and micro levels.

By now, the greatest success was achieved in the development of organic semiconductor materials of the n-type based on fullerenes, which basically meet the necessary requirements.[15] Existing approaches to the synthesis of organic semiconductor materials of the p-type do not yet provide a required level of combination of the technological parameters, that stimulates the search for new structures and methods for their synthesis.

The present review is devoted to macromolecular systems with the p-type conductivity of various topology of the main chain: from linear to hyperbranched. By now, a vast amount of such systems have been described in the literature,[1—4] therefore, in this review we will pay attention only to those of them, which possess the most interesting properties from the point of view of practical use.

1. General concepts of organic (polymeric) electronics

In the contemporary literature,[16] a semiconductor is defined as a material exhibiting dielectric properties at low temperatures, but possessing considerable conductivity at room temperature. In essence, a semiconductor is a dielectric, whose band gap is narrow enough for its conduction band to become thermally considerably populated at room temperature. The definition given is true only for the intrinsic semiconductors, whereas electronics frequently uses a possibility to change electronic properties of semiconductors by means of trace amounts of impurities added on purpose, the so-called "doping". Semiconductors with the thus changed properties are called extrinsic.

Figure 1 shows the energy diagram of metals, dielectrics, and semiconductors built in the framework of the band theory for solids and clearly illustrating the differences between intrinsic and extrinsic semiconductors, as well as between the n- and p-type semiconductors. This theory describes metals as substances with a partially filled conduction band, whereas dielectrics as substances with a filled valence band and empty conduction band. In fact, a dielectric is an ideal insulator only at 0 K, whereas partial transition of electrons from the valence band to the conduction band occurs with the temperature elevation, which makes the dielectric to acquire electrical conductivity. It should be noted that the thermal energy is very low, therefore, the thermally induced conductivity is observed only for the substances with a narrow band gap, which are called the intrinsic semiconductors.[17] As to the doping process, the presence of an impurity in the system leads to the emergence of additional localized energy levels close to the conduction band (the n-type doping) or to the valence bands (the p-type doping). Therefore, the energy necessary for the transition of an electron (hole) to the conduction band (valence band), considerably decreases down to the level attainable due to the thermal energy.

The principal difference of organic semiconductors from inorganic consists in the fact that this high extent of purity, as for inorganic substances, is unattainable for them, therefore, impurities of both the p- and the n-type are present in any organic semiconductor. Such semiconductors are called compensated and are the closest to the intrinsic semiconductors in their behavior. External doping of organic semiconductors can be achieved only due to the addition of large amounts of a dopant (in the order of several percent as compared to the parts per million for pure silicon). This leads to the transition already to the conducting state, rather than to semiconducting, that changes in principle the character of their use in electronic devices. Therefore, nowadays an alternative way for addition of a charge carrier to the organic system is used for semiconductors: by charge injection from metallic elec-

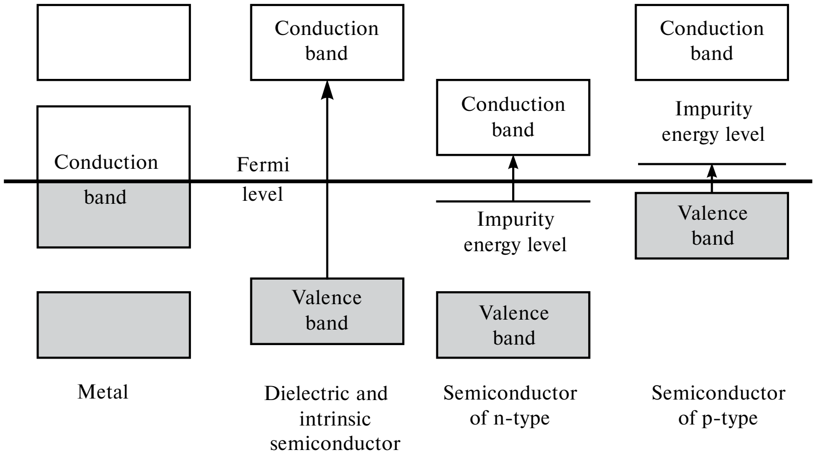


Fig. 1. Energy diagram of metals, dielectrics, and semiconductors.

trodes. Varying the electrode metal (*i.e.*, virtually its Fermi level), as well as gate dielectric, it can be possible to obtain semiconductors of both the p- and the n-type based on the same organic substance.[18] Therefore, for each specific electrode any organic semiconductor can possess conductivity predominantly either of the p-, or the n-type depending on its band gap and its position with respect to the Fermi level of this electrode. At the same time, since a number of standard metals, as a rule, are used as test-electrodes, most often gold or aluminum with the work function of 5.1—5.47 eV and 4.06—4.26 eV, respectively (depending on the surface crystallographic orientations[19]), majority of stable semiconductor polymers exhibit the p-type conductivity under these conditions.

2. Means to control a band gap

Materials for modern electronic and optoelectronic devices should possess not only good semiconductor characteristics, but also required optical properties, appropriate absorption and luminescence spectra, as well as a controlled energy gap width. It is known that the band gap of linear π-conjugated polymeric system is determined by the sum of five components:[4]

$$E_g = E_{BLA} + E_{res} + E_{Sub} + E_\theta + E_{Int},$$

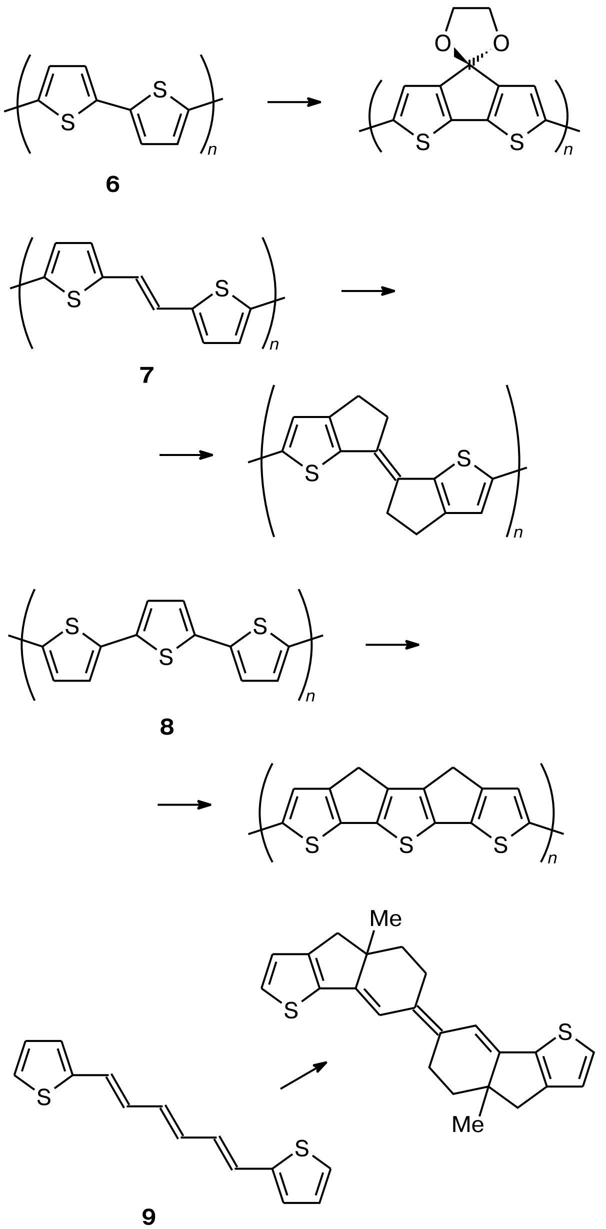
where E_{BLA} (BLA stands for bond length alternation) is related to the different chemical bond lengths in the conjugated system, interfering the full delocalization of electrons, E_{res} is the resonance energy, which is determined by energy nonequivalence of aromatic and quinoid forms in aromatic conjugated system, E_{Sub} is determined by the presence of electron-donating or electron-withdrawing substituents in the aromatic ring, E_θ is determined by the dihedral angle between neighboring rings, E_{Int} is determined by the intermolecular interaction.

Starting from this, the following principal synthetic means for the control of the band gap can be highlighted:

1) incorporation of double bonds between aromatic rings, which leads to a decrease in the degree of the system aromaticity (a decrease in E_{res}), as well as to the removal of steric interactions between neighboring aromatic rings, *i.e.* to planarization of the system. Thus, going from poly(thiophene) to poly(thiophenevinylene) the absorption maxima are shifted by 50 nm to the red region (from 440 to 490 nm), that corresponds to a decrease in E_g by 0.3 eV (see Ref. 20);

2) an increase in the rigidity of the conjugated chain due to additional covalent binding, which leads to planarization of the whole system and considerable increase in efficiency of photoluminescence. This effect has been illustrated using bithiophene (**6**),[21] dithienylethylene (**7**),[22] terthiophene (**8**),[23] dithienylhexatriene (**9**),[24] oligothienylenevinylene,[25] and fluorene as examples (Scheme 1);

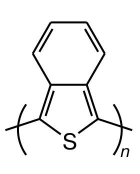
Scheme 1



3) incorporation of electron-releasing or electron-withdrawing substituents into the main chain. For instance, introduction of a dicyano or keto group at position 3 of the thiophene ring or to the vinylene fragment of poly(thienylethylene) leads to a decrease in E_g to 1.5 eV as compared to E_g = 2 eV for poly(thiophene).[26] Addition of electron-releasing groups, such as alkyl, alkoxy, or alkylsulfanyl groups, also leads to a decrease in the band gap, though with lower efficiency than on introduction of electron-withdrawing groups;

4) an increase in the percentage of the quinoid form due to the fussion of the thiophene ring with the aromatic systems of higher resonance energy. Among such systems

are poly(benzo[*c*]thiophene) (E_g = 1.10 eV) (**12**),[27] poly(dihexylthieno[3,4-*b*]pyrazine) (E_g = 0.95 eV) (**13**),[28] poly(thieno[3,4-*b*]thiophene) (E_g = 0.80—0.90 eV) (**14**);[29]



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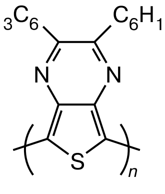

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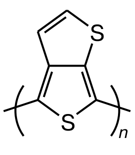

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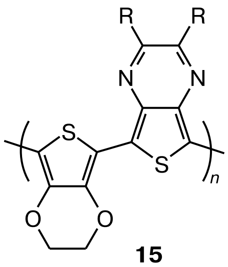
5) alternation of electron-releasing and -withdrawing groups, leading to the widening the valence and conduction bands and finally to the narrowing the band gap;[30]

6) synergetic combination of structural effects, allowing one to decrease E_g to 0.36 eV (the value was obtained for the alternated copolymer of 3,4-ethylenedioxythiophene and thienopyrazine) (**15**).[31]



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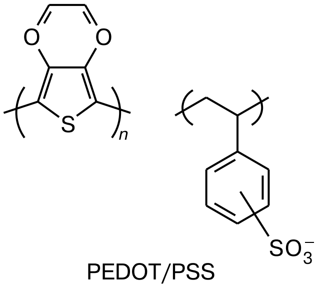
A considerable disadvantage of such systems is that they are virtually insoluble in most organic solvents. Introduction of a dodecyl substituent into the ethylenedioxythiophene fragment improves the solubility, but considerably increases E_g (to 0.80 eV) and significantly decreases thermooxidative stability of the copolymer.[32]

The described approaches to the control of the band gap allowed one to obtain polymers which found their practical use in electrochromic devices of various colors (derived from poly(ethylenedioxythiophene)), light-emitting diodes with high quantum yield of electroluminescence, and solar cells with the power conversion efficiency up to 5.5% (see Ref. 33).

The complex of poly(3,4-ethylenedioxythiophene) with poly(4-styrenesulfonic acid) (PEDOT/PSS), which is a well soluble conducting system with a wide range of application, deserves special attention.[34]



PEDOT/PSS

This complex is widely used in auto, power, and electronic industries for the preparation of antistatic and electroconducting coatings, as well as transparent electrode in the sensor displays, OLEDs, electrochromic devices, electronic paper, *etc.*[35] Special attention deserves a method for obtaining submicron structures from this polymer based on differences in dewetting described by Sirringhaus and coauthors.[36] It consists in the removal of a possibility for certain regions of the substrate to be wetted with aqueous drops of a conducting polymer deposited by the jet printing method, using prior deposition of templates with different surface energies on the substrate (Fig. 2). The use of this method allows one to obtain nano-scaled OTFT devices with conductivity close to the conductivity characteristic of OTFT on the micron scale.

3. Polymeric (linear) systems

3.1. Poly(thiophenes)

Materials based on thiophene, readily available from raw organic product of treatment of coal and oil shale or reprocessing of oil waste, possess the highest potential among donor semiconducting polymers. Poly(thiophene) itself, which can be obtained, for example, by polymerization of 2,5-dibromothiophene in the presence of nickel(II) cyclooctadiene complex and triphenylphosphine in DMF in virtually quantitative yield, is insoluble in organic solvents and due to this cannot be used as material for the production of any devices on its basis.[37]

The solubility of poly(thiophenes) can be significantly improved by introduction of various substituents (most often, *n*-alkyl) at position 3 of the thiophene ring, for example, by preparation of the corresponding monomer by the Kumada reaction from 3-bromothiophene and the corresponding alkylmagnesium halides.[38] Poly(3-alkylthiophenes) (P3AT) are soluble in organic solvents, possess good film formation and semiconductor properties. They have a high potential for possible applications as functional layers of organic thin-layer transistors, light-emitting diodes, solar cells (in the combination with acceptor semiconducting materials, for example, fullerenes), *etc.*

However, oxidative polymerization and metal catalyzed cross-coupling of 3-alkylthiophenes most often lead to polymers of irregular structure. In particular, a widely used oxidative polymerization in the presence of iron(III) chloride can lead to both insoluble poly(thiophene)[39] and well soluble regioirregular poly(3-alkylthiophenes). Such a polymerization results in obtaining[40] polymers with relatively high molecular weights (20000—400000 g mol^{-1}) and polydispersity indices ranging from 1.3 to 5. Unfortunately, regioirregular poly(3-alkylthiophenes) possess low hole mobility due to the limited length of the π-conjugation resulted from nonplanar conformation of the neighboring thiophene rings bonded by the "head-to-head" type.

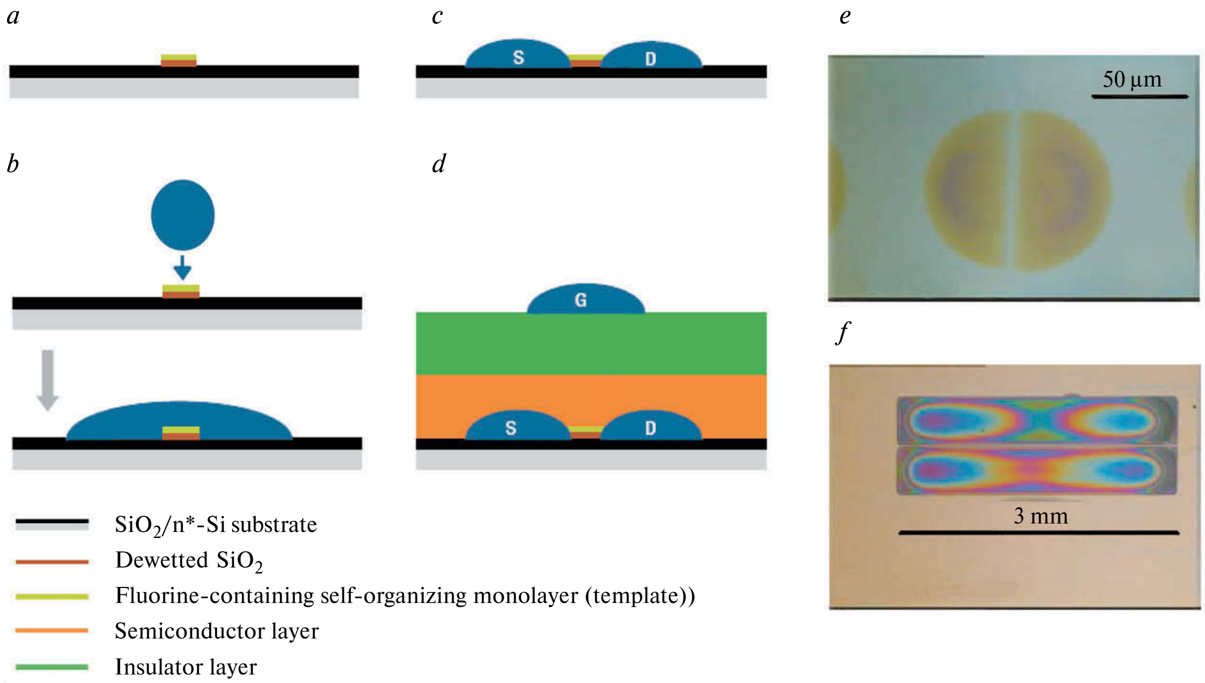
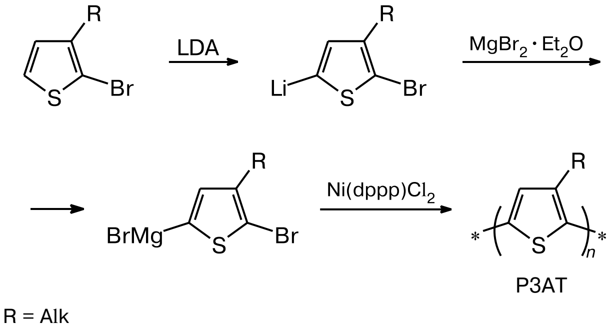


Fig. 2. Schematic picture of the dewetting process (*a*—*d*): *a* is the template deposited on the silicon support, *b* is the deposition of an aqueous drop of PEDOT/PSS by the inkjet printing method on the template, *c* is the dewetting process of the drop deposited, *d* is the structure of the polymeric transistor obtained by dewetting, *e*, *f* are the microphotographs of the structures formed depending on the dewetting conditions: *e* is the aq. solution of PEDOT/PSS = 1 : 1 deposited by the jet printing method, the template width is 500 nm, the SiO_2 layer is 30 nm thick, *f* is the aq. solution of PEDOT/PSS = 1 : 3 deposited by the dip-coating method, the template width is 5 μm) (see Ref. 36).

Note. Fig. 2 is available in full color in the on-line version of the journal (http://www.springerlink.com).

It should be noted that molecular design allows one to obtain stereoregular poly(3,3″-dialkylterthiophene)[41] and poly(3,3″-dialkylquaterthiophene)[42] based on the same oxidative polymerization reaction.

Scheme 2

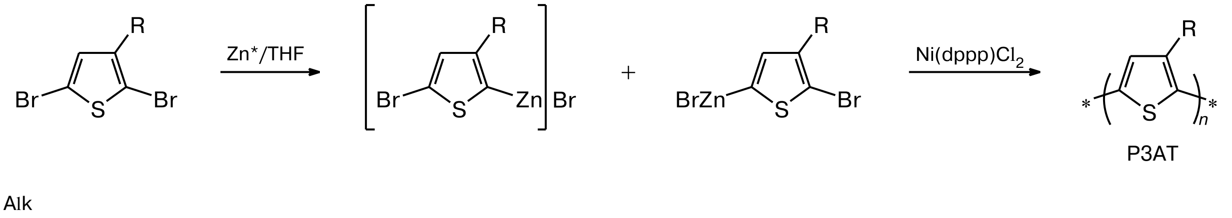


Synthesis of structurally homogeneous (with the "head-to-tail" regioregularity) poly(3-alkylthiophene) according to Scheme 2 was a significant step forward (see Ref. 43). The degree of regioregularity of the polymers obtained varied from 93% for *n*-butyl substituents to 98% for *n*-hexyl. Afterwards, this reaction was modified by the replacement of lithiation of 2-bromo(3-alkyl)thiophene with LDA with the reaction of 2,5-dibromo(3-alkyl)thiophene with methylmagnesium bromide, that allowed one to obtain the Grignard reagent in one step (the Grignard metathesis — GRIM-polymerization)[44]. It should be noted that the use in the reaction of a nickel catalyst (in contrast to palladium, which is frequently used in this reaction as well) leads to polymerization by the mechanism of a "living chain", that gives a possibility to obtain mono- and bifunctional polymers with different terminal groups, including aldehyde, hydroxy, or amino groups, allowing one to control morphology of the polymers synthesized due to the self-assembly of the terminal groups on various surfaces, as well as opens ways for the synthesis of block and grafting copolymers.[45] In one of the latest works of this group of authors, a versatile character of the Grignard metathesis was demonstrated for the synthesis of other conjugated polymers, such as poly(fluorenes), poly(pyrroles), and poly(carbazoles).[46]

The use of highly active "Rieke zinc" instead of organomagnesium derivative in the reaction in Scheme 3 also allows one to obtain regioregular poly(3-hexylthiophene).[47]

Another two widespread approaches to the synthesis of highly regioregular poly(3-alkylthiophenes) (the degree of

Scheme 3



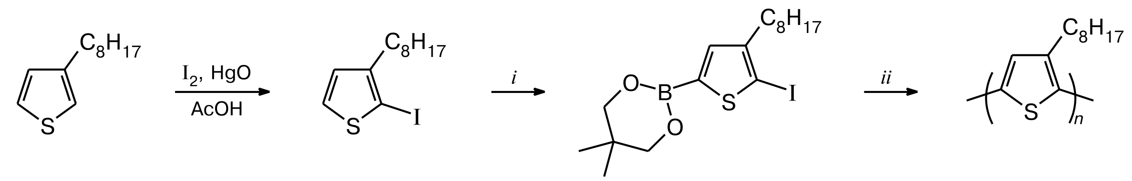
regioregularity is 96—97%) are based on the Suzuki (Scheme 4)[48] and Stille (Scheme 5)[49] cross-coupling reactions. The former is based on the reaction of 5-organoboron derivatives of 3-alkyl-2-halothiophene or 2,5-dihalo- and 2,5-diorganoboron derivatives of thiophene in the presence of a palladium catalyst and a base[50] (see Scheme 4). The Stille cross-coupling includes reaction of thiophene 2,5-dihalo- and 2,5-diorganotin derivatives in the presence of a palladium catalyst (see Scheme 5).[51]

It is obvious that the change in tacticity of the main macromolecular chain of poly(thiophenes) will influence their properties. For instance, it was found that upon increase in the degree of regioregularity of poly(3-hexylthiophene) (P3HT) from 54 to 97%, the hole mobility increases from 0.01 to 0.4 cm^2 (V s)$^{-1}$, respectively.[52] The study of a dependence of the charge carrier mobility on the length of an alkyl substituent (from 4 to 12 carbon atoms) for regioregular poly(3-alkylthiophenes) showed that *n*-hexyl is the optimum substituent due to the best self-organization of poly(3-hexylthiophene) as compared to other polymers of this series.[53]

In contrast to the pseudoliving GRIM-polymerization, the Suzuki or Stille polycondensation reactions usually lead to polymers of not very high molecular weight, possessing wide polydispersity. However, it was shown[49] that an increase in the molecular weight (M > 15000) and considerable decrease in polydispersity index ($M_w/M_n = 2$) of the poly(thiophenes) synthesized can be reached by the Stille addition upon irradiation with microwaves for 10 min.

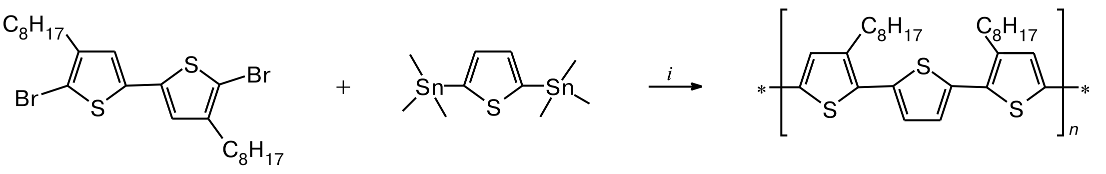
Ability for the charge transport and quality of the thin-layer transistors obtained based on poly(thiophenes) strongly depend not only on chemical structure of the polymeric system, but also on the presence of the long-range order in the polymeric film. Therefore, it is necessary to control a degree of the structural ordering, in particular, orientation of the polymeric chains in the thin films obtained. There exist various approaches for the ordering chains in the polymeric films, such as temperature annealing,[54] stretching,[55] deposition by the Langmuir—Blodgett method,[10] method of polishing[56] and nanopolishing,[57] change in the rate of the support spinning during spin-coating,[58] as well as chemical grafting of

Scheme 4



Reagents and conditions: *i*. 1) LDA, THF, –40 °C, 40 min; 2) $B(OMe)_3$, –40 °C → 20 °C; 3) H^+, H_2O; 4) 2,2-dimethyl-1,3-propanediol, Na_2SO_4, Et_2O. *ii*. $Pd(OAc)_2$, K_2CO_3, THF, EtOH, H_2O, 16 h.

Scheme 5



i. Pd(0), μW

poly(thiophenes) on a support, for example, by the Kumada reaction,[59] and others.

Special attention should be paid to the self-assembling method of oligo- and poly(thiophene) fragments on different supports. In the work,[60] a self-assembled monolayer field-effect transistor (SAMFET) with the long-range order intermolecular π—π-interaction in the monolayer is described. The close-packed arrangement was reached due to the use of liquid-crystalline molecules consisting of the π-conjugated mesogenic groups, separated with a long aliphatic spacer from the monofunctionalized "anchor" groups.

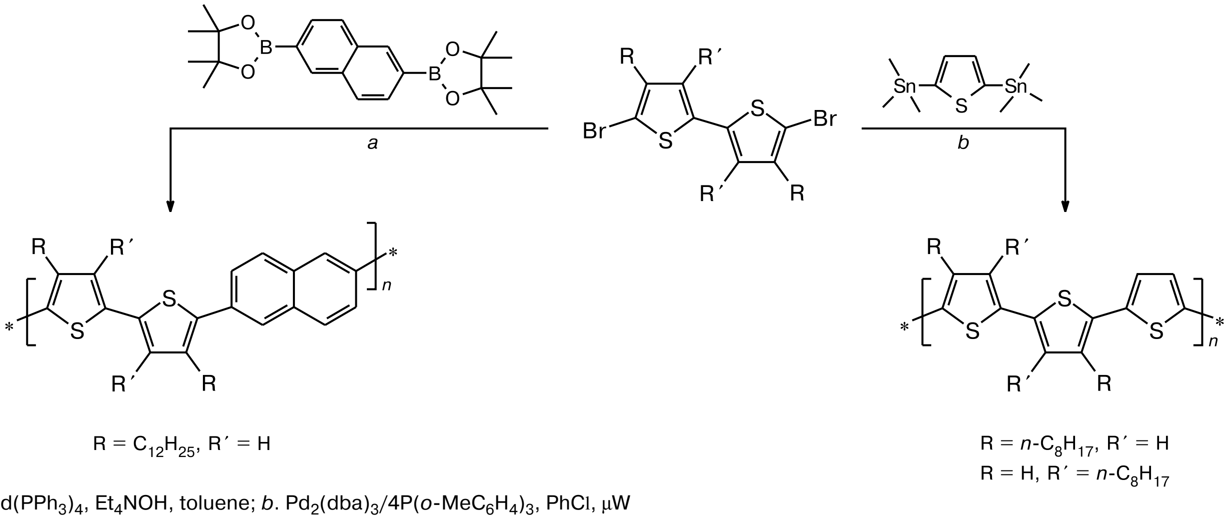
A principal disadvantage of the completely conjugated poly(3-alkylthiophene) systems consists in the fact that their semiconductor properties under normal conditions (in air, in the presence of oxygen and moisture) are considerably worse than in an inert atmosphere (or under reduced pressure) due to the doping the poly(thiophene) with the air oxygen. The oxidative stability of poly(thiophenes) can be increased by increasing their ionization potential, which, in addition to other factors, depends on the effective length of the π-conjugation in the main polymeric chain. Several approaches to restrict the π—π-overlap between adjacent thiophene rings are described in the literature: (1) steric (due to the head-to-head regioregular introduction of the side 3-alkyl substituents into thiophene ring),[7] (2) by enhancement of the main polymeric chain free rotation due to the introduction of β-unsubstituted thiophene units in the structure of the chain,[42] or (3) introduction of a nonconjugated comonomer into the polymeric system.[61]

Terthiophene polymers have been synthesized by the Suzuki or Stille cross-coupling ([A + B]-copolymerization)[7] (Scheme 6). The poly(terthiophenes) obtained had molecular weights from 9000 to 30000, high degrees of crystallinity and melting points (125—212 °C). Their absorption maxima were found in the range 401—463 nm (in toluene solution) and 426—560 nm (in the solid phase). The thin-film transistors prepared on their basis possessed hole mobility of $1 \cdot 10^{-5}$—$3 \cdot 10^{-2}$ cm^2 (V s)$^{-1}$ and the on/off ratio of 10—$4 \cdot 10^4$. All the transistor parameters remained relatively stable under normal conditions for at least 15 days. Another approach to obtaining poly(3,3″-dialkylterthiophenes) consists in the oxidative polymerization of the corresponding monomers in chlorobenzene in the presence of iron(III) chloride.[41] Such poly(terthiophenes) are regiosymmetric and have a tendency to intermolecular ordering with the formation of lamelar π-stacking structures (Fig. 3) and efficient π-conjugation in the system.

Enhancement of the main chain free rotation has been accomplished by a group of Canadian scientists,[42] synthesized a new class of regioregular poly(3,3‴-dialkylquaterthiophenes) (Scheme 7), which possess not only enough oxidative stability, but also good solubility, high charge carrier mobility (to 0.14 cm^2 (V s)$^{-1}$), and high on/off ratio (higher than 10^7). The AFM images of the thin films of such quaterthiophenes, obtained after annealing at 145 °C and subsequent cooling, demonstrate clearly seen well ordered domains formed from the rod-shaped structures; the domain sizes are (30—100)×(10—15) nm (see Ref. 42).

Another example of systems stable under normal environmental conditions is heterocyclic regiosymmetric copolymer of thieno[2,3-*b*]thiophene with 4,4'-dialkyl-2,2′-bithiophene[61] (Scheme 8) synthesized by the Stille cross-coupling and also possessing good solubility, high charge carrier mobility (to 0.15 cm^2 (V s)$^{-1}$), and sufficient on/off ratio (in the order of 10^5). In contrast to the polymers described above, the structure of this polymer includes the thieno[2,3-*b*]thiophene units, which cannot provide long

Scheme 6



a. Pd(PPh$_3$)$_4$, Et$_4$NOH, toluene; *b*. Pd$_2$(dba)$_3$/4P(*o*-MeC$_6$H$_4$)$_3$, PhCl, μW

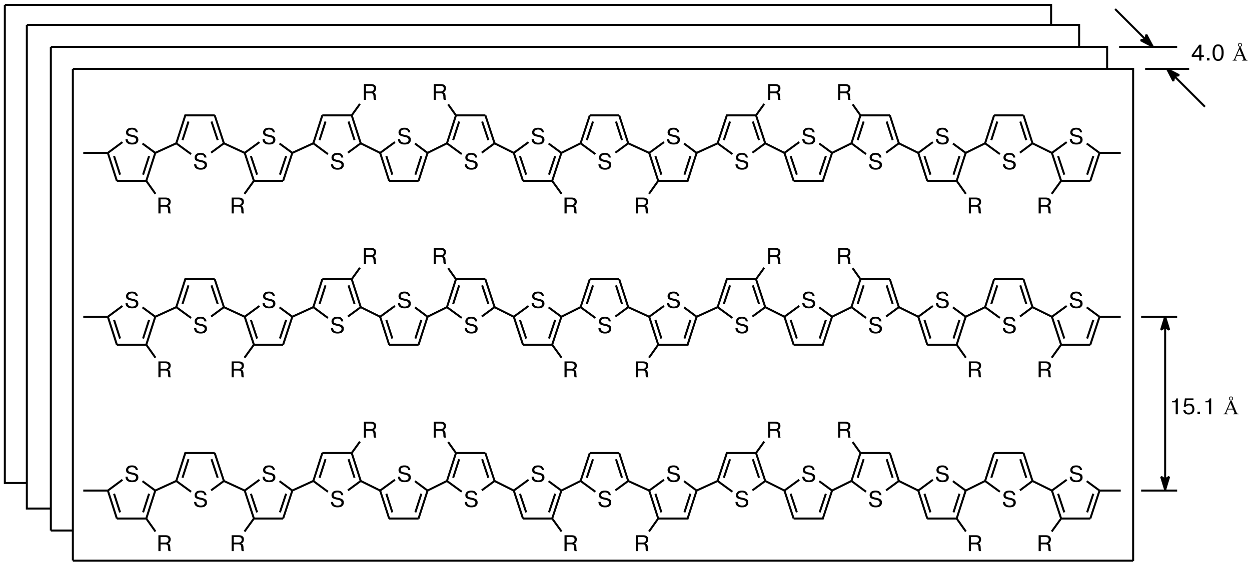
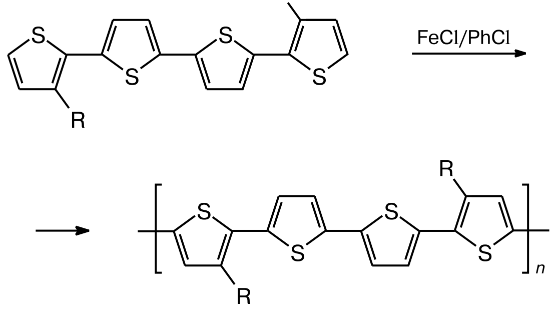


Fig. 3. Schematic picture of lamellar structures formed by regiosymmetric poly(thiophenes) due to the intermolecular interaction of the side chains.

Scheme 7



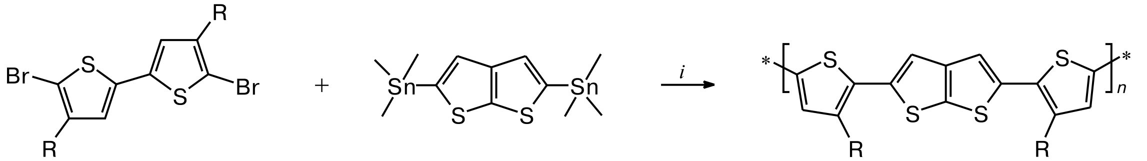
conjugation between thiophene units bound to it, thus restricting conjugation of the macromolecular chain and increasing ionization potential of the polymer.

Recently, another approach to the enhancement of oxidative stability of poly(thiophenes) due to the regioregular introduction of electron-withdrawing dodecyl carboxylate substituents into the thiophene ring by the Stille cross-coupling has been described.[8] Transistors obtained from such materials in the presence of atmospheric oxygen possess high hole mobility (0.06 $cm^2 (V s)^{-1}$), high on/off ratio (higher than 10^5), retaining the initial characteristics at least for several months.

High values of the charge carrier mobility were reached for liquid-crystalline regioregular poly{2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-*b*]thiophenes}, where decyl, dodecyl, and tetradecyl groups were used as the alkyl substituents.[62] The thienothiophene polymers synthesized with number average molecular weight of 28500—33000 and polydispersity index of 1.8 had melting points of 244—251 °C, possessed hole mobility of 0.22—0.63 $cm^2 (V s)^{-1}$, and retained their characteristics at least for 25 days under conditions of atmospheric air with low humidity (4%).

Recently, it was shown that poly- and oligo(thiophenes) are prospective materials for the use not only in OTFT, but also in OPV (solar cells). For instance, the power conversion efficiency in the two-layer photovoltaic cell using quinquethiophene with terminal dicyanovinyl substituents in combination with fullerene reached 3.4% (see Ref. 63). Yet better results (power conversion efficiency up to 4.5—5%) were obtained for bulk heterojunc-

Scheme 8



i. $Pd_2(dba)_3/4P(o\text{-}MeC_6H_4)_3$, PhCl, μW

$R = C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}$

tion solar cells based on the combination of fullerene with poly(3-hexylthiophene).[64] Further improvement of characteristics is related to the development of donor polymers with a narrow band gap (less than 2 eV), capable of light absorption in wide range of wavelengths. In particular, in the work[65] the power conversion efficiency of 6.5% is reported for the tandem solar cells, where poly(3-hexylthiophene) and copolymer of cyclopentabithiophene alkyl derivative with benzothiadiazole were used as the donor materials.

To conclude this section, it should be noted that poly(thiophenes) are not only good organic semiconductors, but also possess light-emitting properties not typical of other classes of π-conjugated polymers, exhibiting red electroluminescence.[2] However, the efficiency of photo- and electroluminescence of poly(thiophenes) themselves remains low, if other fragments (most often based on phenylene) are not additionally included into their structure either as substituents at position 3 of the thiophene ring, or as comonomers during preparation of the polymers. At present, the best luminescent properties exhibit polymers based on 1,4-phenylenes themselves and their derivatives, in particular, poly(*p*-phenylenevinylenes)[66] and poly(fluorenes).

3.2. Poly(fluorenes)

Alkyl-substituted poly(fluorenes) are yet another important class of conjugated polymers, especially demanded in the new display technologies due to their inherent efficient electroluminescence, high enough charge carrier mobility (up to $3 \cdot 10^{-4}$ cm^2 (V s)$^{-1}$), and good reprocessing properties.

Soluble poly(2,7-fluorene) has been obtained for the first time by oxidative polycondensation of 9,9-dihexylfluorene in the presence of iron(III) chloride.[67] The polymer synthesized possessed rather low molecular weight ($M_n < 5000$, $P_n = 9—13$) and had a number of defects, which did not correspond to the 2,7-substitution.

Development of efficient catalysts based on transition metals opened the way to the synthesis of structurally homogeneous poly(fluorenes) of high molecular weight. At present, the following synthetic pathways are widely used:

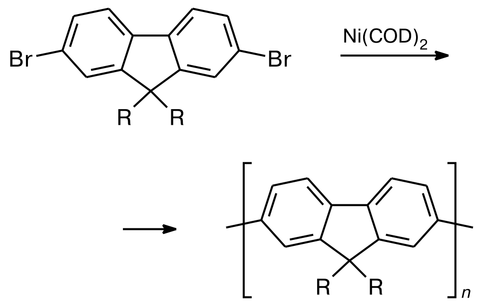
1) reductive aryl—aryl cross-coupling of dihaloaryls by the Yamamoto reaction (Scheme 9);[68]

2) aryl—aryl cross-coupling of aryldiboronic acids (or their esters) and dihaloaryls by the Suzuki reaction (Scheme 10, X = $B(OH)_2$, $B(OR)_2$, under basic conditions);[69]

3) aryl—aryl cross-coupling of distannylaryls and dihaloaryls by the Stille reaction (Scheme 10, X = SnR_3).[70]

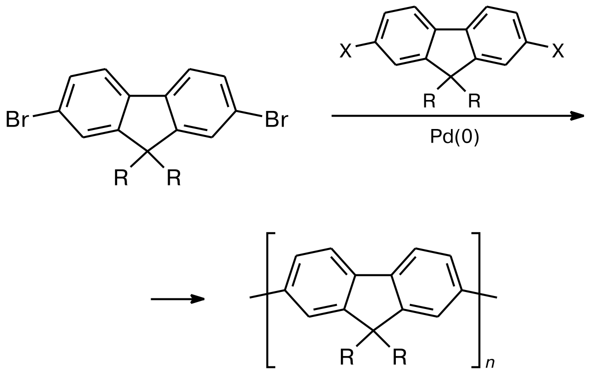
It is known that poly(fluorenes) obtained by the Suzuki reaction, as a rule, possess molecular mass in the order of 10^4, whereas addition by the Yamamoto reaction conditioned by a thorough purification of starting monomers allows one to obtain polymers with M_n up to $2 \cdot 10^5$.

Scheme 9



R = Alk

Scheme 10



X = $B(OH)_2$, $B(OR)_2$, SnR_3

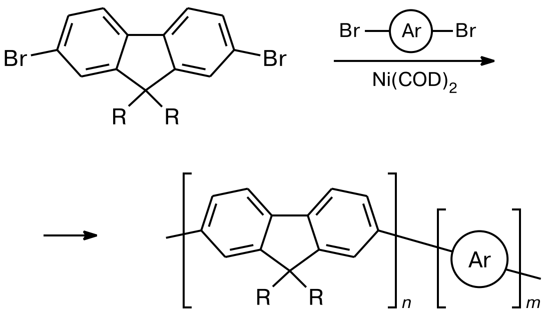
Poly(9,9-dialkylfluorenes) with the length of the alkyl substituent more than six carbon atoms are well soluble in organic solvents and do not precipitate during synthesis. It was shown[3] that the structure of alkyl substituent virtually has no influence on the optical and electronic properties of poly(fluorenes) in a dilute solution, however, it determines the polymer structure in the solid phase. Poly(fluorenes) with *n*-alkyl substituents exhibit tendency to aggregation in the condensed state (form a β-phase, characterizing by additional absorption peak shifted to the red region), whereas behavior of polymers with branched alkyl substituents in the solid phase is the same as in a dilute solution (have one absorption maximum at 380 nm).

It should be noted that for the synthesis of poly(fluorenes), it is necessary to use highly pure starting materials, since even low amounts of monoalkylated (9-alkylfluorene) derivatives lead for the centers of oxidative destruction to emerge (keto-defects) and considerably worsen properties of polymers obtained (undesirable green-blue luminescence was observed instead of pure light blue).[71]

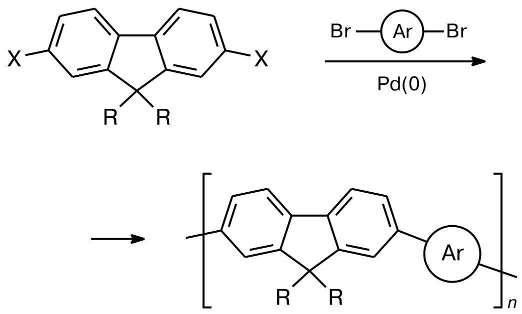
Poly(9,9-dialkylfluorenes) exhibit liquid crystalline properties and form nematic mesophase, making polyfluorene films to be prospective materials for the accomplishment of monodomain ordering with high dichroism coefficient on absorption (up to 15) or with highly polarized photo- and electroluminescence (degree of polarization up to 15, intensity up to 45 cd m^{-2} for the voltage of 19 V).[72]

Chemical structure of poly(fluorenes) can be changed by copolycondensation with various comonomers (Schemes 11 and 12). Introduction of monofunctional comonomers (Scheme 13) leads to emergence of a certain amount of terminal functional groups in the polymer structure, that allows one to improve electrical, optical, electroluminescent, and other properties of the starting fluorenes. For instance, introduction of styrene or triarylamine terminal groups improves hole conductivity of poly(fluorenes), which, in turn, improves their electroluminescent characteristics.[73]

Scheme 11



Scheme 12

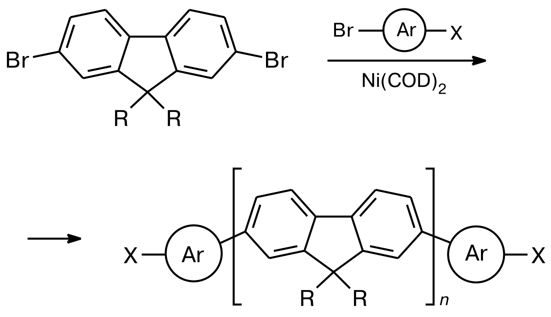


X = B(OH)$_2$, B(OR)$_2$, SnR$_3$

The use of difunctional monomers allows one to obtain various copolymers based on fluorene. In this case, addition by the Yamamoto reaction (see Scheme 11) leads only to statistical copolymers,[74] whereas cross-coupling by the Stille or Suzuki reaction (see Scheme 12) using comonomers with various functionality results in the synthesis of strictly alternated copolymers.[75]

Thus, copolymerization of fluorenes with 1,3,4-heterodiazoles leads to the loss of liquid-crystalline properties and obtaining soluble semiconductors with predominant conductivity of the *n*-type,[76] as well as to the change in the luminescent spectral characteristic. In particular, incorporation of benzothiadiazole derivatives into the polyfluorene structures allows one to displace the luminescence spectrum to the red region and to obtain light-emitting polymers with irradiation chromaticity ranging from green to yellow green (525—534 nm).[77] Copolymerization with 1,4-phenylene does not virtually affect the fluorescence spectral characteristics, but increases its quantum yield from 79% to 87%, whereas copolymerization with 9,9-alkoxyfluorenes decreases the quantum yield to 16% (see Ref. 78).

Scheme 13



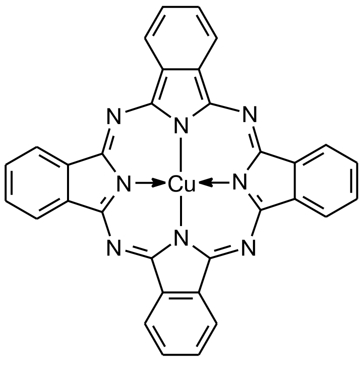
X = NH$_2$, NPh$_2$

A specific feature of linear π-conjugated polymeric systems is the anisotropy of optical and electrical properties due to the chain rigidity of such macromolecules, therefore, a thorough control of their molecular orientation in the process of production of different devices is required. Such a situation is a considerable problem for obtaining films from solution or upon their printing. One of possible solutions for this problem is development of branched and hyperbranched (semi)conducting macromolecular systems, possessing isotropic electronic and other properties on the surface or in the volume, respectively.

4. Branched (two-dimensional) systems

Phthalocyanines (**16**) are the first example of two-dimensional (2D) planar π-conjugated systems, proved the most efficient materials for multi-layer solar cells.[79]

Among planar discotic molecules, the following representatives are of great interest: triphenylene derivatives **17**, capable of self-organization to columns and possessing conductivity inside the column with hole mobility in the range 0.01—0.1 cm^2 (V s)$^{-1}$ (see Ref. 80), hexabenzocoronenes **18** with charge carrier mobility higher than 1.0 cm^2 (V s)$^{-1}$ in crystal and about 0.5 cm^2 (V s)$^{-1}$ in the LC-phase,[81] and hexazatrinaphthylenes **19** with mobility in the range 0.3—0.9 cm^2 (V s)$^{-1}$ (see Ref. 82).



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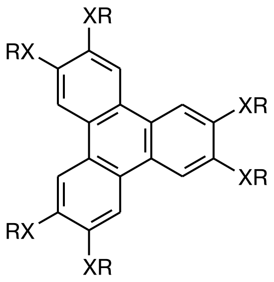
Photovoltaic cells with quantum efficiency ~3% obtained by co-precipitation of dialkoxytriphenylene (donor) and perylenediimine (acceptor) are also described in the literature,[83] they are films with vertical segregation of the donor-acceptor layers.

In addition to the liquid-crystalline discotics, of interest also are the star-shaped two-dimensional π-conjugated systems consisting of oligothiophene fragments bonded to benzene (**20**—**22**),[84] truxene (**23**—**25**),[85] or benzotrithiophene (**26**)[86] cores.

In the case of benzene ring, the branched macromolecules obtained possessed better solubility and film formation properties as compared to the low-molecular-weight



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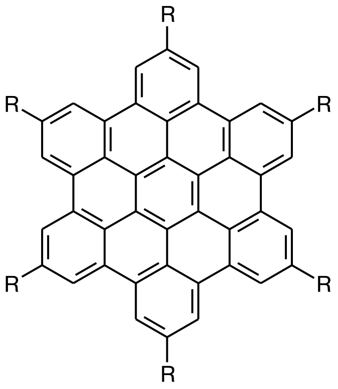

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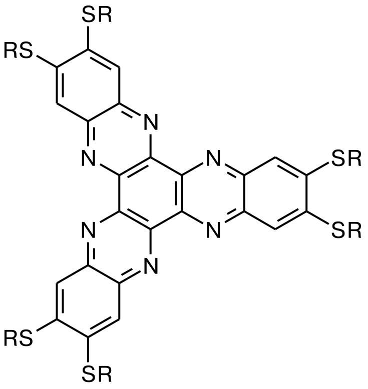
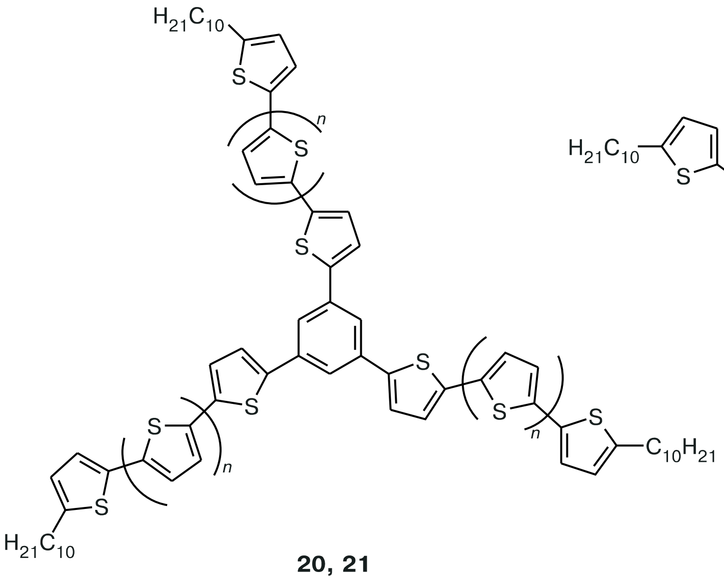


19

17: X = S, O
18: R = n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, n-$C_{14}H_{29}$
19: R = n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$



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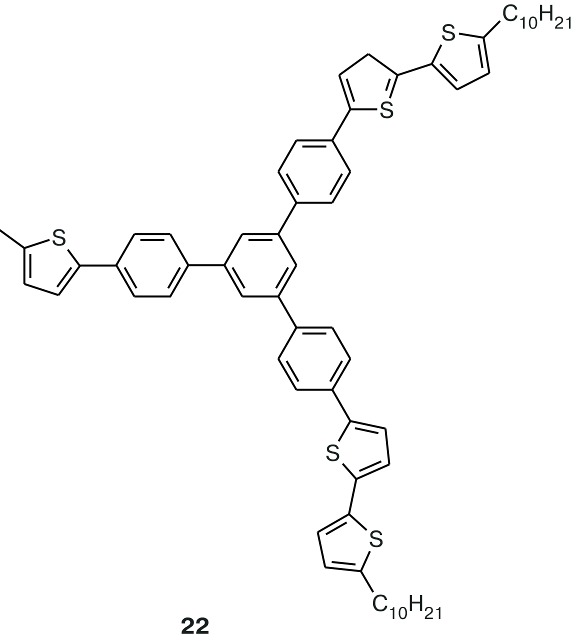

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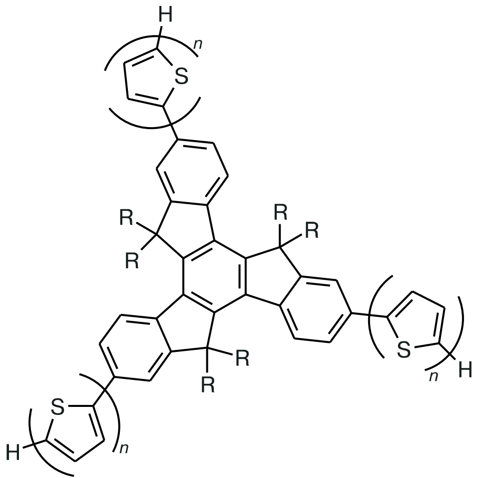
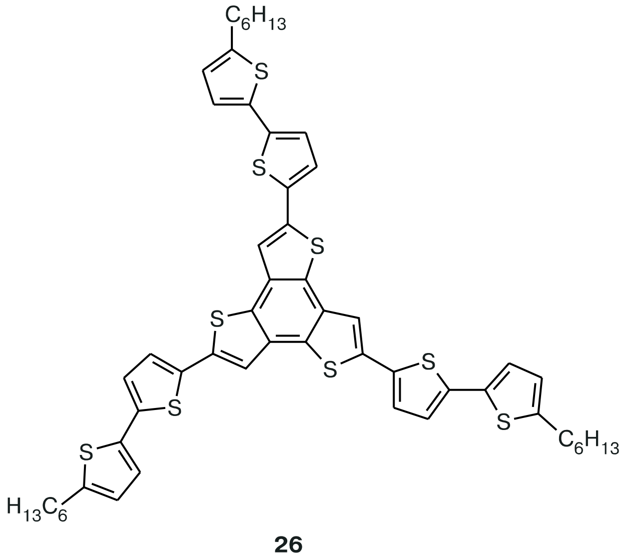
20, 21: n = 0 (**20**); n = 1, $\mu = 2 \cdot 10^{-4}$ cm^2 (V s)$^{-1}$ (**21**)



23—25



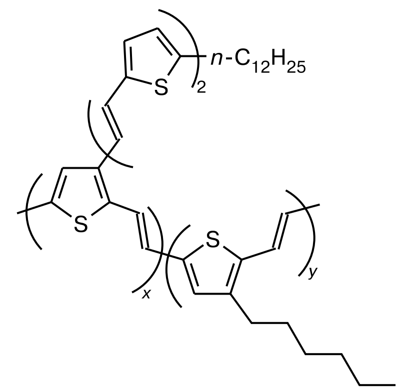
26

23—25: $n = 0$, $\mu = 1.03 \cdot 10^{-3}$ cm^2 (V s)$^{-1}$ (**23**); $n = 1$ (**24**), 3 (**25**)
26: $\mu = 2 \cdot 10^{-4}$ cm^2 (V s)$^{-1}$

analogs and exhibited hole mobility in the order of $2 \cdot 10^{-4}$ cm^2 (V s)$^{-1}$, which considerably decreased with the decrease in the length of the thiophene fragment or upon displacement of one thiophene ring with 1,4-phenylene one[84]. In the case of truxene ring, the hole mobility reached $1 \cdot 10^{-3}$ cm^2 (V s)$^{-1}$, decreasing with the increase in the length of the thiophene fragments[85]. It should be noted that branched macromolecules based on benzene (**22**) and truxene (**23—25**) are nonplanar, since in the case of benzene a dihedral angle exists between the neighboring phenyl rings, limiting the extent of conjugation, whereas in the case of truxene the terminal hexyl substituents are bonded to the carbon atom having the sp^3-hybridization and are not placed in the plane of the molecule, interfering close π—π-interaction[85].[85]

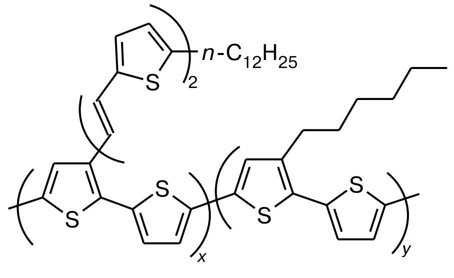
A strict planar conformation was achieved for oligo(thiophenes) based on benzothiophene core **26**. It was shown that molecules of such thiophenes are oriented parallel to the substrate plane, that leads to an increase of the absorption coefficient by a factor of 3 as compared to its linear analog. Power conversion efficiency of OPV cells obtained on their basis increased from 0.40% to 18% going from linear to branched systems on the maximum absorption wavelength and from 0.04% to 0.8% upon irradiation with white light.[86]

Another approach to the development of two-dimensional conjugated systems consists in addition of side conjugated substituents to the main, also conjugated, polymeric chain. Various copolymers of poly(thienylenevinylene) **27** and poly(thiophene) **28** with side thienylenevinylene groups are described.[87,88] In all the cases, the addition of conjugated side groups led to the broadening the absorption range and, respectively, to the improvement of the light-absorbing properties. The power conversion efficiency in solar cells based on such copolymers is 0.32% for poly(thienylenevinylene) and more than 3% for poly(thiophene).



27

$x : y = 0.35$ (**27**), $x : y = 0.59$ (**28**)



28

5. Hyperbranched (three-dimensional) systems

Three-dimensional (3D) (semi)conducting systems can be divided into two main classes with regard to the macromolecule structures: irregular, which include branched and hyperbranched polymers, and regular, which include star-shaped molecules based on triphenyleneamine, spiro-linked molecules, molecules with tetrahedron geometry, and dendrimers.

The work[6] described the synthesis of branched polymers based on thiophene and consisting of nonregioregular poly(3-octylthiophene) segments (OT) bound to trithienylbenzenes of various functionality (from 3 to 6) with average weight molecular masses from 70000 to 200000 (Fig. 4). Measurements of hole mobility showed its increase by two orders of magnitude as compared to the linear nonregioregular poly(3-octylthiophenes) (to 10^{-4} cm^2 (V s)$^{-1}$). In addition, an enhancement of the red

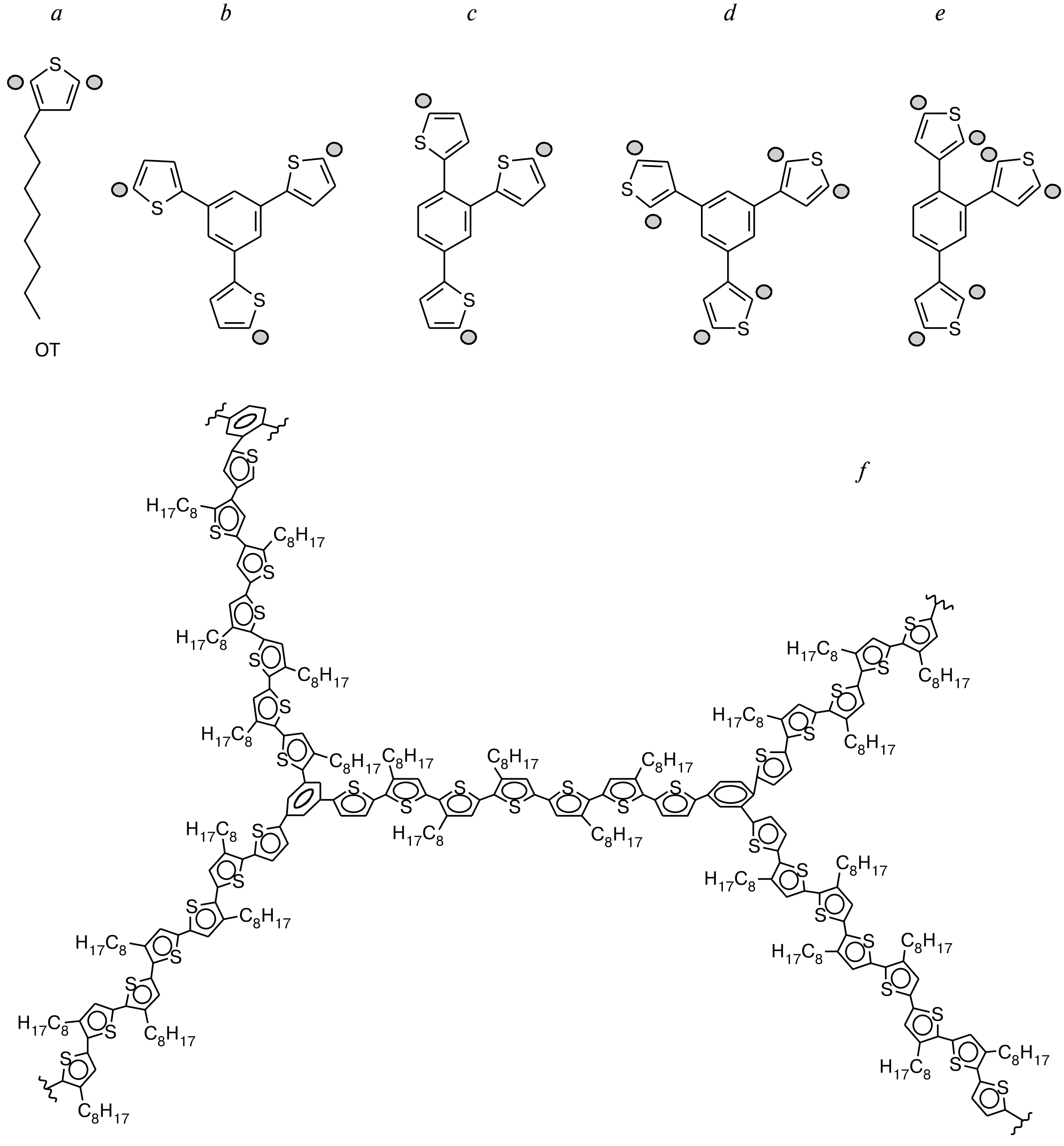


Fig. 4. Polymers based on 3-octylthiophene (*a*) and trithienylbenzenes of various functionality: 3 (*b*, *c*) or 6 (*d*, *e*), as well as schematic structure of the branched polymer based on 3-octylthiophene and 1,2,4-tris(2-thienyl)benzene (*f*).

shift was observed going from a dilute solution to the films obtained by the spin-coating method (to 0.41 eV as compared to the 0.09 eV for the corresponding linear systems).

Unsymmetric hyperbranched poly(thiophenes)[89] are another example of three-dimensional systems. Such poly(thiophenes) absorb light in a wide range of wavelengths (220—520 nm), exhibit strong fluorescence with the maximum at 550 nm, and demonstrate efficient intramolecular energy transfer.

Conducting systems based on triphenylamine (TPA) are the intermediate class between planar and three-dimensional systems and due to the steric interactions between phenyl groups have nonplanar propeller-like shape. By now, a large number of systems consisting of the TPA core with linear π-conjugated substituents, such as fluorenyl (**29**), carbazole (**30—32**), thienyl (**33**), and selenophenyl (**34**), as well as phenylthienyl (**35**) and phenylselenophenyl (**36**) groups,[90,91] have been synthesized.

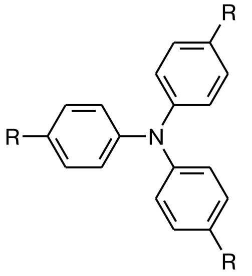
The maximum hole mobility in such systems was obtained for the selenophene and thiophene substituents and reached $1.5 \cdot 10^{-2}$ and $1.1 \cdot 10^{-2}$ cm^2 (V s)$^{-1}$, respectively. The maximum power conversion efficiency in OPV cells was in the case of *n*-hexylthiophene substituents and reached 0.32%.

The literature describes a number of hybrid donor-acceptor systems based on TPA. Regioregular oligo(3-alkylthiophenes) (with the number of thiophene rings from 2 to 6) with terminal perylenimine substituents (**37**)[92] or thienylenevinylene fragments with terminal indanedione (**38**) or dicyanovinyl (**39**) groups[93] were used as substituents.

Power conversion efficiency in such systems was 0.25, 0.80, and 2%, respectively. In addition, compounds with terminal dicyanovinyl groups proved suitable for the preparation of red OLED with high spectral purity.

Spiro-linked conjugated molecules, represented in the literature by such examples as spirooctaphenyl and oligomers of ter(9,9-diarylfluorenes),[94] are amorphous materials with high glass transition temperatures and high efficiency of photoluminescence in the solid state and possess conductivity of both the *p*- and the *n*-type (with the charge carrier mobility of $4 \cdot 10^{-3}$ and $1 \cdot 10^{-3}$ cm^2 (V s)$^{-1}$, respectively).

Hybrid 3D systems based on TPA and spirobifluorene **40—43** are also described, as well as properties of light-emitting diodes and solar cells produced from them.[95]



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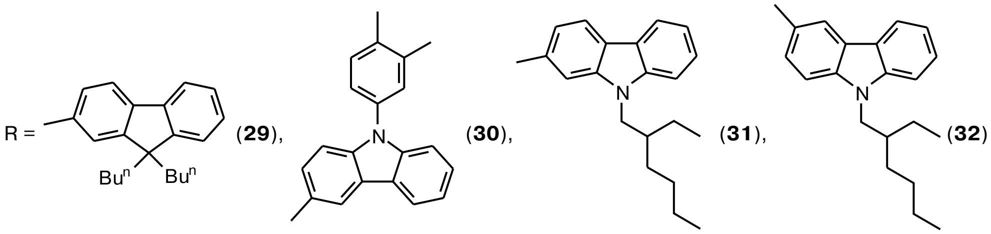

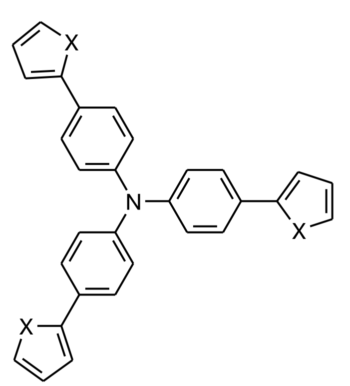

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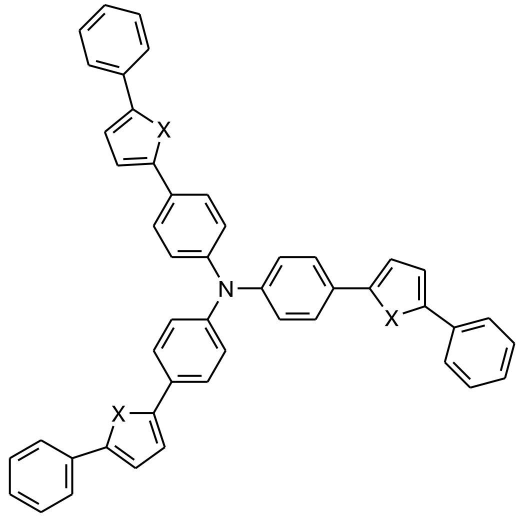
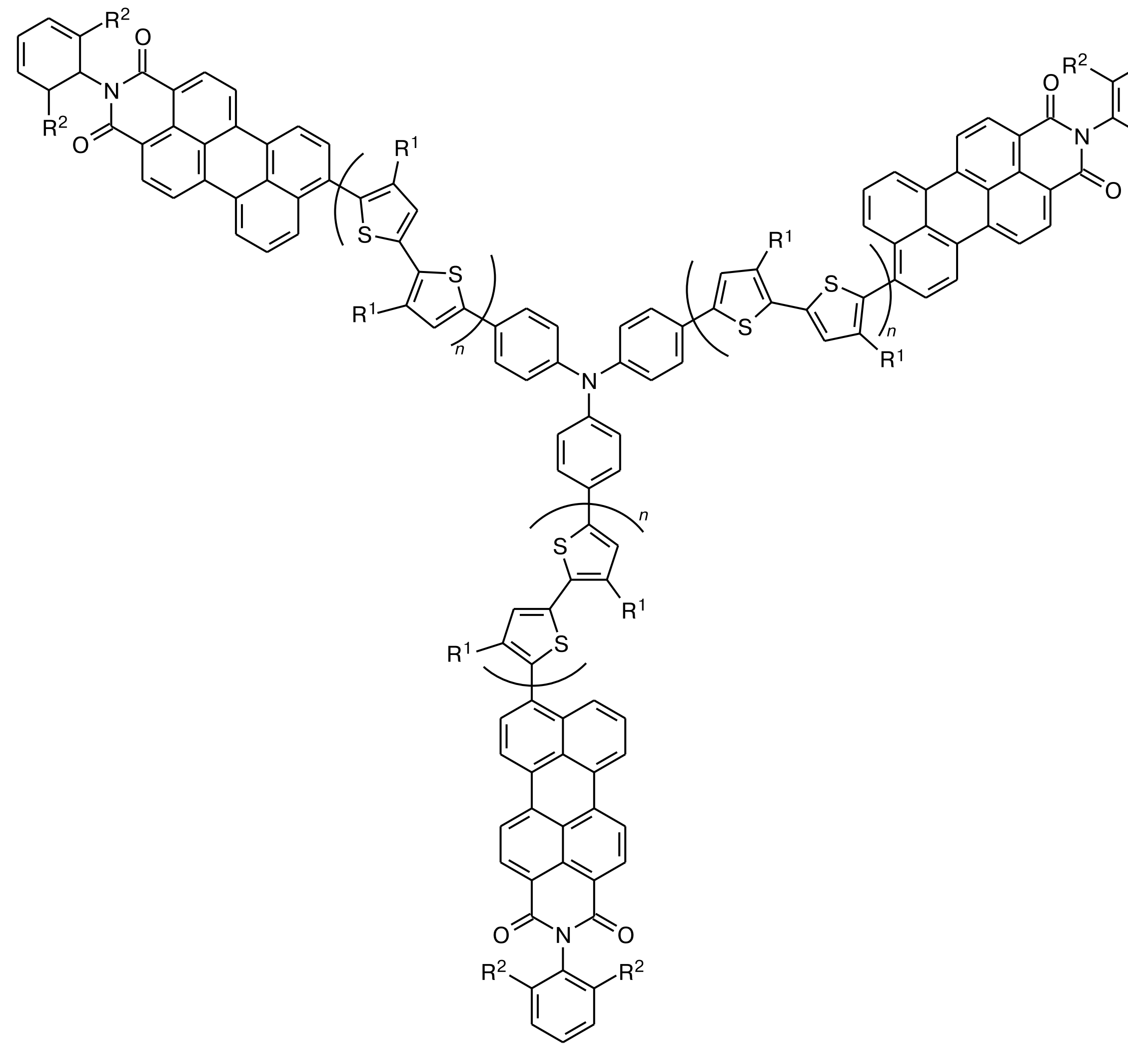


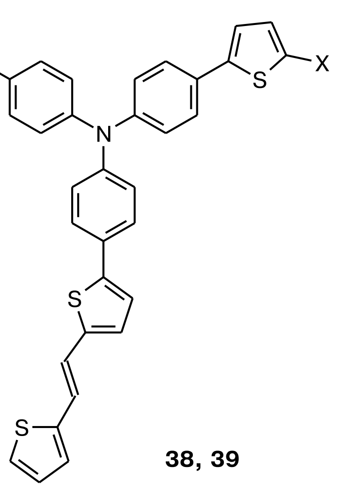
35, 36

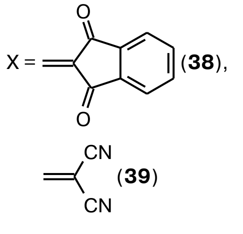
X = S (**33**, **35**), Se (**34**, **36**)



R^1 = *n*-hexyl, R^2 = Pr^i, *n* = 1—3

37





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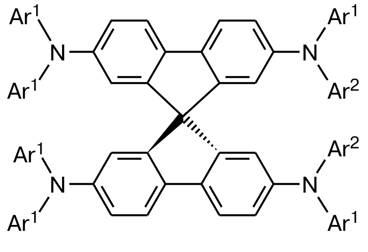
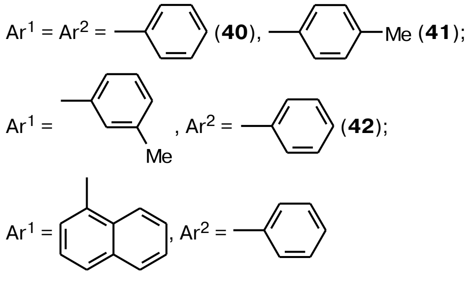


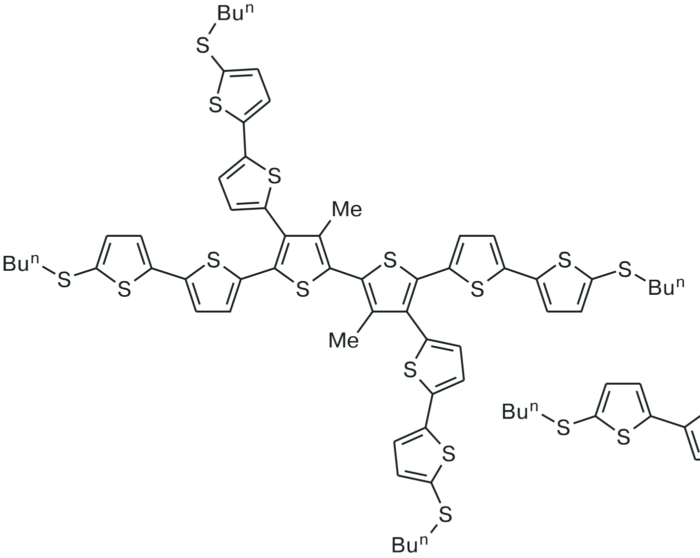
40—43



It was found that such materials possess relatively low hole mobility as compared to their linear analogs ($7 \cdot 10^{-5}$ cm^2 (V s)$^{-1}$), however, high on/off ratio and very good stability during a long period of time under normal conditions.

In the last years, a lot of reports are devoted to the synthesis of conjugated systems with tetrahedral geometry based on tetraphenylmethane,[96] tetraphenylsilane,[97] tetraphenyladamantane[97] cores or silicon atom[98] with phenylenevinylene,[97] oligo(*p*-phenylene),[99] naphthalenediimine,[100] or oligo(thienyl)[101] substituents. On the whole, such systems possess higher charge carrier mobility and higher power conversion efficiency as compared to their linear analogs.

Dendrimers are alternative approaches to the obtaining (semi)conducting materials with isotropic electronic properties. In the last years, various oligo(thiophene)-containing dendrimers based on bithiophene (**44**, **45**),[102—104] benzene (**46**, **47**),[105] as well as silicon (**48**),[106] as the branching center have been synthesized.



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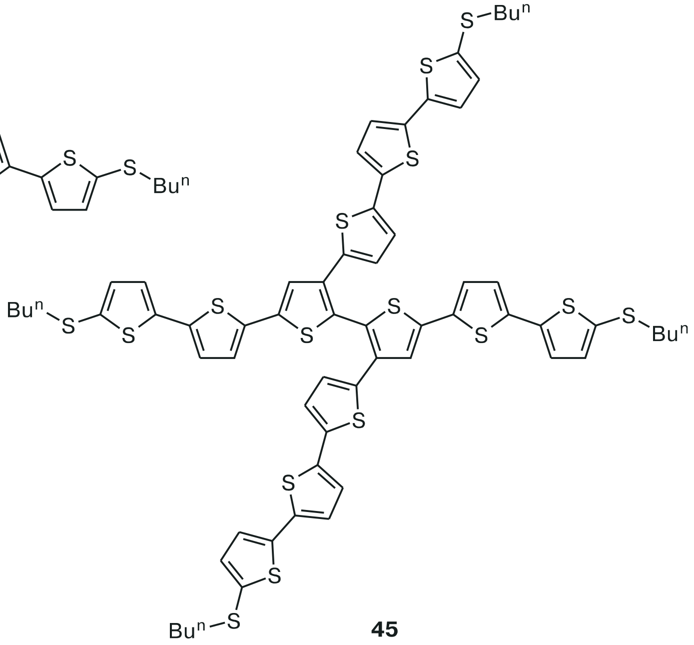

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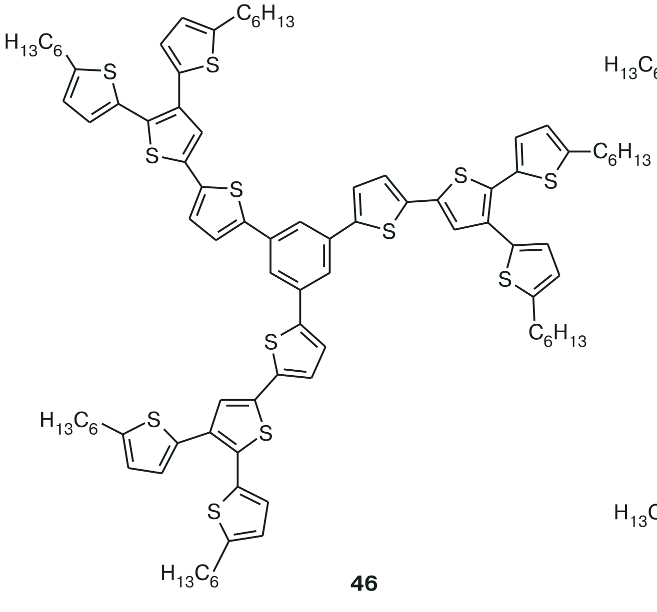

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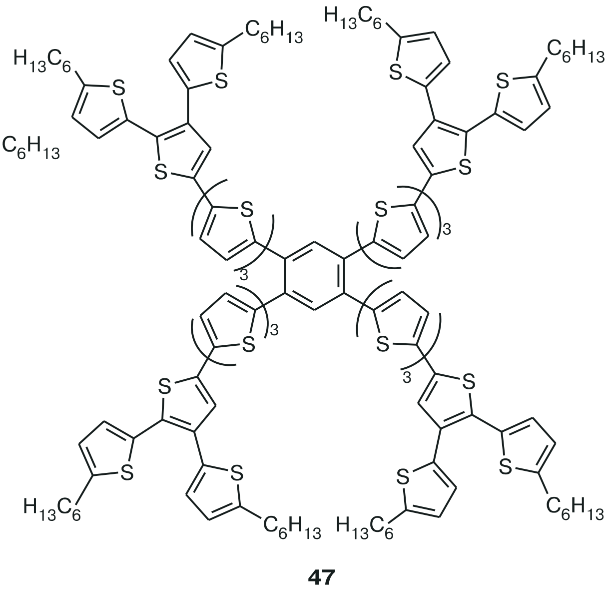

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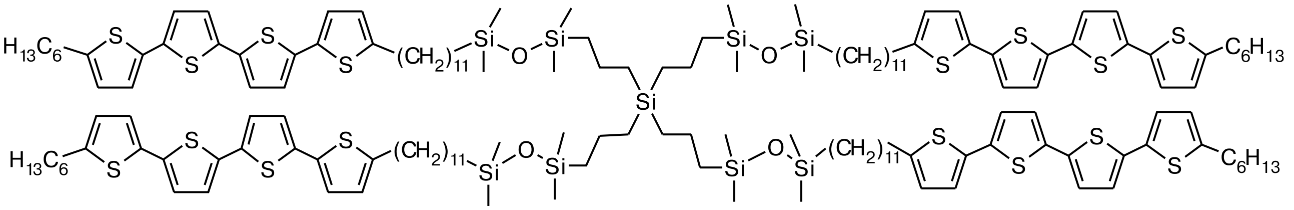

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The maximum hole mobility reported for such systems was $2 \cdot 10^{-2}$ cm^2 (V s)$^{-1}$, whereas the power conversion efficiency upon irradiation with white light was up to 1.30%. The results obtained are yet worse than the maximum reachable for poly(3-hexylthiophene), however, these are only the first materials synthesized based on the branched monomers and further optimization of devices based on such systems is very prospective.

Conclusion

Examples given above demonstrate intensive development of this field in the last decade, which already resulted in obtaining great variety of macromolecular structures possessing the *p*-type conductivity. They are, first of all, classic one-dimensional macromolecules consisting of conjugated aromatic or heteroaromatic rings. Variations in conditions for the synthesis and the starting monomers allow one to obtain soluble homo- and copolymers of various chemical structure, regulate their molecular-mass characteristics, and microstructure of the polymeric chain, which determines electrical, optical, thermal, and other properties of materials obtained from them. However, the very nature of such rigid-chain macromolecules predetermines the anisotropy of their properties and related to it necessity to optimize and thoroughly control morphology of materials obtained in order to improve their charge transport properties. This considerably complicates production process and, therefore, the final cost of organic electronics devices made of them, such as thin-film transistors, light-emitting diodes, photovoltaic cells, *etc*. Possible approach to solve the problem of anisotropy of organic semiconductor materials is development of two- and three-dimensional macromolecular systems, whose conductivity should depend less or not at all from their processing method. The first steps in this direction have been already done: a number of planar and three-dimensional macromolecules have been constructed, which in their characteristics are not inferior to and sometimes exceed their linear analogs. Research in this direction is only at the beginning, therefore, new interesting results in this field can be expected.

Examples considered in this review determine two the most prospective approaches to the improvement of properties of macromolecular system with the p-type conductivity. The first approach suggests a search for new possibilities to control morphology of thin films of one- and two-dimensional semiconducting materials on the nano- and microlevels in order to obtain as highly organized mono- and polylayers as possible. To accomplish this pathway, there are very promising both physico-chemical approaches to the ordering the thin films (annealing, mechanical stretching, formation of LC-phase, ordering in the Langmuir layers or due to the capillary forces) and chemical approaches, consisting in the introduction in their structures of functional groups assisting in the self-organization of such materials in the thin films due to the interaction with a substrate. The second pathway consists in the design of new three-dimensional organic semiconducting systems with the isotropic distribution of the charge carrier mobility in the bulk and development of simple synthetic ways for the creation of such systems. Both irregular (hyper)branched polymers and regular star-shaped systems, such as dendrimers and molecules with tetrahedral geometry, can be called prospective three-dimensional systems. Special attention in the design of organic semiconducting systems deserves silicon. First, chemistry of organosilicon compounds suggests wide synthetic possibilities in obtaining various regular hyperbranched structures possessing semiconductor properties, as well as allows one to obtain ordered self-assembling films on solid substrates or on the interfaces. Second, the presence of silicon atom in the semiconducting chain in a number of cases leads to specific electronic effects due to additional conjugation of the π electron system of (hetero)aromatic units with the silicon d-electrons.

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