Research Article

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Research in the Field of Organic Photovoltaics at the Institute for Problems of Chemical Physics of Russian Academy of Sciences

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Abstract: In the present review we highlight the main research activities in the field of organic photonics and photovoltaics at the Institute for Problems of Chemical Physics of Russian Academy of Sciences (IPCP RAS). Extensive investigation of optical and electrical properties of π-conjugated organic compounds performed at IPCP RAS since 1960’s resulted in design of many exciting materials representing organic semiconductors, metals and superconductors. Organic Schottky barrier and p/n junction photovoltaic devices constructed at IPCP RAS in 1960’s and 1970’s were among the first examples of reasonably efficient organic solar cells at that time. These early discoveries inspired younger generations of the researchers to continue the work of their mentors and explore the world of organic materials and photonic devices such as molecular photonic switches, organic light emitting diodes, solar cells, photodetectors, photoswitchable organic field-effect transistors and memory elements.

Keywords: IPCP RAS, organic solar cells, organic photovoltaic cells, organic electronics, molecular electronics, molecular switches, photodetectors, field-effect transistors, memory elements, OLEDs

1 Introduction

The history of organic electronics and photonics is considerably longer than we usually assume. In the middle of 19th century Henry Letheby investigated the electrochemical and chemical oxidation products of aniline in acidic media and observed the formation of electrically conductive substance which was most probably polyaniline[1]. Later on in 1891 polyaniline was synthesized and characterized by F. Goppelsroeder[2]. Subsequent research resulted in observation of a noticeable electrical conductivity in doped organic solids [3, 4]. Particularly exiting was the observation of a high electrical conductivity in a doped polyacetylene[5–8] and superconductivity in poly(sulfur nitride) (SN)n in 1970s [9]. Discovery of semiconductor and metallic properties of ionic salts derived from tetrathiafulvalenes (TTFs) initiated intensive exploration of the substances named later as organic or synthetic metals [10, 11]. The same family of the materials gave birth to the first truly organic superconductors discovered by K. Bechgaard in 1980 [12].

Very similar studies were performed at that time at the Institute of Chemical Physics in Moscow and its branch in Chernogolovka (currently the Institute for Problems of Chemical Physics of Russian Academy of Sciences, IPCP RAS) which were among the leading research centers in the USSR [13]. In particular, the first normal-pressure organic superconductors were discovered at IPCP RAS in early 1980s [14, 15]. This research direction was developed later by many research groups [16].

Organic semiconductors were also intensively investigated all over the world [17–19, 21–24]. Some particularly exciting results were obtained at the Institute for Chemical Physics, E. L. Frankevich and his colleagues reported in 1960s the influence of magnetic fields on the photoconductivity [25, 26] and electroluminescence [27] of single crystals of organic semiconductors. This was a revolutionary discovery giving birth to the Reaction Yield Detected Magnetic Resonance (RYDMR). Interested reader might follow a review discussing these effects [28]. A similar technique was used in early 1980s for investigation of photoinduced charge separation in the systems comprising organic dyes such as chlorophyll and fucoxanthin [29, 30], conjugated polymers and organic donor-acceptor blends [31–33]. Some other researchers reported the synthesis and electrical conductivity of polyacetylene in early 1960s [6, 7], studied behavior of organic semiconductors under ra-
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Radiation [34], and investigated charge generation and transport in natural photosynthetic systems [35].

Organic solar cells attracted considerable attention of the researchers since 1950s [36]. The first single layer Schottky barrier devices based on organic semiconductors demonstrated very low power conversion efficiencies (<< 1%) and external quantum yields. Among different types of investigated at that time photoactive organic materials, porphyrins and phthalocyanines are the most interesting since they resemble natural photosynthetic antenna. Single layer photovoltaic devices based on different phthalocyanines were constructed at IPCP RAS by V. A. Benderskii et. al. in 1960s and 1970s [37–39]. Extensive purification of metal-free phthalocyanines resulted in preparation of single crystals demonstrating high drift mobilities of 0.2-0.7 cm²·V⁻¹·s⁻¹ (for both holes and electrons) and well-pronounced photoeffect [40]. Doping of metal phthalocyanines with oxygen, sulfur or selenium was applied in order to fabricate p/n junction devices which showed reasonable power conversion efficiencies of ~0.1-0.5% [41–43]. It was also revealed that in thin polycrystalline phthalocyanine films doped with oxygen charge carriers are generated by singlet exciton dissociation at the oxygen impurity centers with quantum yields close to unity [16, 19], which resembles the behavior of modern donor/acceptor systems. Further improvement was achieved 7-15 years later by C. Tang who invented double-layer p/n junction devices comprising two principally different organic semiconductor materials (p- and n-type) which showed power conversion efficiencies of ~1% [44].

Some research groups at IPCP RAS contributed to the design, structural and spectroscopic characterization of photochromic and thermochromic compounds, molecular photoswitches, photoswitchable organic ferromagnets and other types of exciting materials [45–50]. Special attention was paid to design of novel materials for photography [51, 52], exploration of colloidal systems including gold nanoparticles and quantum dots based on inorganic semiconductors such as CdS, CdSe and PbS [53, 54]. Nanostructured systems based on inorganic semiconductors have been investigated as promising materials for solar cells [55–57]. Several families of transition metal complexes, aromatic polyamines and polymers were designed as promising materials for organic light-emitting diodes (OLEDs) [58–61].

The given above examples illustrate that Institute for Problems of Chemical Physics of Russian Academy of Sciences has been contributing significantly to the development of organic photonics and photovoltaics in Russia and in the world since early 1960s. In the present review we will focus in more detail on the research activities of our group (Laboratory for Multifunctional Materials and Organic Electronics) at IPCP RAS most closely related to organic photovoltaics. In particular, we will discuss the main results obtained during the last decade in the frame of our successful collaboration with other research groups in Russia and European Union.

2 Fullerene derivatives bearing chelating pyridyl groups for bilayer and multicomponent organic solar cells.

Fullerenes and their derivatives have attracted a particular attention as highly promising acceptor components for construction of numerous photoactive molecular systems. Especially exiting were different molecular and supramolecular ensembles comprising porphyrins and phthalocyanines resembling closely natural photosynthetic antenna [62]. Molecular complexes of non-functionalized fullerenes with porphyrins were thoroughly investigated at IPCP RAS by D. Konarev et. al. [63] In order to construct supramolecular fullerene-porphyrine and fullerene-phthalocyanine photoactive systems our group has developed an efficient synthetic route for preparing various pyridyl-substituted pyrrolidinofullerenes (Scheme 1) [64].

This route resembles in some way classical Prato reaction [65], but amino acids are replaced with picolylamines and pyridyl group is not cleaved like COOH in amino acids when pyrrolidine ring is formed. The remarkable feature of the revealed reactions was their excellent stereoselectivity. Pure cis-isomers of 2',5'-disubstituted pyrrolidinofullerenes were formed when primary picolylamines were used as reagents. On the contrary, the application of secondary picolylamines resulted in exclusive formation of trans-isomers of 1',2',5'-trisubstituted pyrrolidino-fullerenes. Stereochemistry of these products has been proved unambiguously using NOESY NMR experiments and x-ray single crystal diffraction [44, 66]. The applica-

![Scheme 1](https://via.placeholder.com/150)

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A large family of pyridyl-substituted pyrrolidinofullerenes has been synthesized using the developed approaches. Molecular structures of some compounds are shown in Fig. 1. These compounds represent fullerene-based ligands which can form complexes with transitional metals as well as metallated porphyrins and phthalocyanines. Such complexes have been isolated and characterized by x-ray single crystal diffraction and spectroscopic techniques [69, 70]. Fig. 2 shows molecular structures of 1:1 complex of pyrrolidinofullerene with zinc tetraphenylporphyrin (ZnTPP) and 1:2 complex of other pyrrolidinofullerene with manganese tetraphenylporphyrin (MnTPP). These complexes were shown to be photoactive: excitation of the donor porphyrin results in a fast electron transfer to the acceptor fullerene derivative [71, 72].

Very similar complex formation and facile photoinduced charge separation was observed for pyridyl-substituted pyrrolidinofullerenes (PyFs) and zinc phthalocyanine (ZnPc) [73]. Such behavior was utilized for construction of diffusion bilayer solar cells [74, 75]. To fabricate such cells, a concentrated PyF solution was spin-coated on the top of the evaporated ZnPc layer. Investigation of the obtained bicomponent systems showed that ZnPc becomes partially dissolved under the fabrication conditions which results in the formation of a diffusion bilayer architecture with the intermediate layer composed of coordination complexes PyF...ZnPc arranged in between the layers of pristine PyF and ZnPc materials (Fig. 3). On
Figure 4: Schematic layouts of multicomponent solar cell illustrating sequence of the deposited layers (left side), charge generation and transport in the device (right side) and formation of self-assembled complex PyF···ZnPc at the interface between the layers (middle) (a); IPCE spectra of multicomponent cells illustrating significant improvement in the photocurrent generation upon addition of PyF (b). Reproduced with permission from [57].

On the base of these findings it was suggested that PyF forms self-assembled coordination complexes at the interface between the top blend layer and underlying ZnPc film and these complexes mediate efficiently charge generation and transport at the interface. The power conversion efficiency of the first multicomponent cells was around 2.0%. Replacement of MDMO-PPV with poly(3-hexylthiophene) (P3HT) improved the efficiency of these devices up to 3.5% providing balanced photoresponse in the 300-800 nm spectral region [78].

It should be noted that the reported sensitization of MDMO-PPV and P3HT with ZnPc was among the first examples of ternary or multicomponent blend devices which are under intensive investigation nowadays [79, 80].

3 Fullerene derivatives undergoing self-assembling with conjugated polymers in organic solar cells.

The presented above examples proved that complex formation between the acceptor component (fullerene derivative) and the donor material (ZnPc) might improve photoinduced charge generation and overall photovoltaic performance of the system. Very similar complex formation might occur also between the fullerene derivatives and conjugated polymers. Nowadays it is not surprising to observe intercalation of fullerene derivatives into the polymer lamellar structure [81–84]. Surprisingly, one of the first reports illustrating the strong supramolecular interactions between the fullerene derivatives and conjugated polymers is often not considered [85]. A combined spectroscopy and microscopy study revealed that fullerene derivatives with appended thiophene and furane units (Fig. 5) form supramolecular architectures with P3HT. It was also proposed that the fullerene and the polymer in

the top (blend) and the bottom (ZnPc) layers. Good electronic contacts should be provided between the materials at the interface to achieve efficient charge generation and transport in multicomponent cells. This is why an addition of small amount (1-4% by weight) of PyF to the multicomponent system dramatically improved its photovoltaic performance. Short circuit current and fill factor were particularly increased suggesting better charge generation and transport in the case of PyF-containing devices. This hypothesis was also supported by the IPCE spectra that demonstrated improved photocurrent generation at longer wavelengths (ZnPc region) upon addition of PyF.

As a special type of solar cells as a hybrid combination of planar bilayer and bulk heterojunction devices have been constructed by spin coating a fullerene/polymer blend on the top of evaporated ZnPc film (Fig. 4) [53]. Illumination of this hybrid structure results in the charge generation in the bulk of the top layer and at the interface between the contrary, the reference material PCBM (Phenyl-C61-butyric acid methyl ester) does not dissolve phthalocyanine underlayer and does not form any coordination complexes with ZnPc. Therefore, solution deposition of PCBM on the top of ZnPc gives a truly bilayer device.

The formation of coordination complexes between PyF and ZnPc (Fig. 3c) improved greatly photovoltaic performance of the device which resulted in 1.6% power conversion efficiency. The reference PCBM system yielded only 0.4% efficiency under the same experimental conditions. The IPCE spectra (Fig. 3b) clearly demonstrate superior photocurrent generation in the PyF-based devices. Most probably, supramolecular association of ZnPc and PyF molecules facilitates photoinduced charge transfer from the donor to the acceptor molecule. Dissociation of a supramolecular dyad after charge separation might prevent back transfer and recombination [76].

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Figure 5: Molecular structures of thiophene and furane-appended fullerene derivatives I-III (a); schematic illustration of the complex formation between the compound I and P3HT (b); AFM images of non-annealed and annealed blends of I/P3HT showing power conversion efficiencies of 2.5 and 3.7% in solar cells, respectively (c). Bright regions on the images are supposed to correspond to I–P3HT aggregates. Reproduced with permission from [63].

Figure 6: AFM images of MDMO-PPV/[60]PCBM (1:4 w/w) composite films cast from chlorobenzene (a) and toluene (b). Reproduced with permission from [67].

4 Fullerene derivatives for controlling the active layer morphology in organic solar cells.

The importance of the active layer morphology was first recognized in 2001 for the solar cells based on the MDMO-PPV/[60]PCBM composite. The power conversion efficiency of the devices was increased from 0.9 to 2.5% simply by replacing the solvent used for the active layer casting from toluene to chlorobenzene [86]. In the subsequent study by Hoppe et al. [87] it was demonstrated that MDMO-PPV/[60]PCBM films cast from toluene are rather inhomogeneous and comprise round-shaped distinct features approaching 500-600 nm in size which were later shown to be the PCBM crystallites [88]. On the contrary, films cast from chlorobenzene were much more homogeneous and the cluster size in that case did not exceed 50 nm. Illustrative AFM images recorded for the toluene-cast and chlorobenzene-cast MDMO-PPV/[60]PCBM films are shown in Fig. 31.

It was mentioned above that the charge generation in bulk heterojunction solar cells occurs at the interface between the donor (in this case MDMO-PPV) and acceptor ([60]PCBM) components of the blend. The excitons generated in the active layer have to diffuse to the interface where charge separation takes place. It is known that characteristic exciton diffusion lengths in organic semiconductors typically do not exceed 20 nm [89, 90]. Therefore, the domains of individual materials formed in the blend as a result of the phase separation should not be larger than the exciton diffusion lengths ($L_{ex}$) in these materials. The round-shaped clusters in the case of the toluene-cast MDMO-PPV/[60]PCBM films are at least 25-30 times larger than the typical $L_{ex}$ values. Therefore a vast majority of excitons generated inside these clusters recombine since they cannot reach donor/acceptor interface where charge separation takes place. The situation is much more positive in the case of chlorobenzene-cast films where the average cluster size matches quite well the $L_{ex}$ value. Smaller degree of the phase separation in this case allows the majority of excitons to reach the fullerene/polymer interface and contribute to the charge carrier generation. Improved morphology of the chlorobenzene-cast MDMO-PPV/[60]PCBM blends results in the superior device performances: EQEs approach 50% and light power conversion efficiencies come close to 2.5% [65].

The effect of the phase separation between the photoactive materials on the photovoltaic performance of
Figure 7: Dependence of the solar cell power conversion efficiency and short circuit current density on the lateral size of the clusters revealed in the films using AFM.

Figure 8: Molecular structures of the fullerene derivatives which showed different solubility in chlorobenzene. Solubility values are given in round brackets as maximal concentration of the material which can be dissolved in 1 mL of the solvent.

Figure 9: Optical microphotographs of thin films representing the P3HT blends with the fullerene derivatives 6, 7, 9 and 10.

To control the active layer morphology one might use different solvents [96], processing additives [97, 98], thermal annealing [99] or solvent vapor annealing [100]. We have shown that morphology of the fullerene-polymer blends can be also affected to a large extent by physical properties of the photoactive materials, particularly, their solubility in the solvent used for the film casting. Figure 8 shows the molecular structures of fullerene derivatives which have rather similar electronic properties (HOMO...
Figure 10: Correlation of the short circuit current density (a), open circuit voltage (b), fill factor (c) and power conversion efficiency (d) of organic solar cells with the solubility of the fullerene derivatives blended with P3HT in the photoactive layer of these devices.

Figure 11: Molecular structures of the fullerene derivatives F1-F12 and polymer P1.

It should be emphasized that varying the solvents, applying thermal or solvent vapor annealing, using processing additives and playing with other film processing conditions alter mainly the kinetics of the blend formation. The most direct approach for tuning the active layer morphology is represented by appropriate chemical modification of the donor and acceptor components in order to improve or decrease their miscibility in the solid state [112]. The strongest advantage of this approach is the possibility of controlling the thermodynamics of the fullerene/polymer binary systems. The thermodynamically stable morphology of the fullerene-polymer blends can be preserved for a long time enabling superior operation stability of the devices. This makes a sharp contrast with the listed above approaches which are relying on kinetics of the fullerene/polymer blend formation inducing metastable morphologies in the solid films.

Controlling the active layer morphology by rational design of the fullerene-based acceptor materials has been recently demonstrated by our group in collaboration with LIOS [113]. Regioregular conjugated PPV-PPE copolymer P1 was investigated in combination with a number of cyclopropane fullerene derivatives. The molecular structures of these materials are shown in Fig. 11.

All twelve fullerene derivatives can be represented by a general molecular structure shown in Fig. 11 (right side). The “cycle” in this structure stands for phenyl or 2-thienyl substituents attached to the cyclopropane ring. The number of methylene units between the cyclopropane ring and the ester group (n) changes from 0 to 3. The total number of carbon atoms forming the alkyl chain attached to the car-
Boxylic group was denoted as $m$ and used as an important structural descriptor.

Fig. 12 shows that the short circuit densities, fill factors and power conversion efficiencies of the devices revealed rather clear correlations with the structural descriptor $m$. It is seen from the Fig. 12 that fullerene derivatives bearing butyl chains attached to the carboxylic group ($m = 4$: F3, F9, F12) yielded the best characteristics. The compounds with the shorter ($m = 1-3$) or longer ($m = 5-8$) alkyl chains exhibited inferior performances.

Fig. 13 shows the microscopy images obtained for the composites comprising fullerene derivatives F1 ($m = 1$), F9 ($m = 4$) and F7 ($m = 8$). It is seen from the figure that F1/P1 films are very inhomogeneous and exhibit large clusters approaching 300-400 nm in size. It is known that the exciton diffusion lengths in organic semiconductors do not exceed typically 10-15 nm. Therefore, the excitons generated inside large clusters recombine before reaching the interface with the other material where charge separation occurs. This explains poor photovoltaic performance of the composite comprising F1 ([60]PCBM). Very similar results were also obtained for F10 ([60]ThCBM) and F11 ([70]PCBM). The best performing composite F9/P1 exhibited well-ordered film structure with the characteristic domain size in the range of 10-20 nm which is very close to the optimum for organic bulk heterojunction solar cells. The composite F7/P1 showed rather structureless SEM and AFM images suggesting that the fullerene derivative and the polymer are well intermixed in this system. It is known that insufficient phase separation does not create percolation pathways required for efficient transport of the photogenerated charges to the electrodes.

The obtained data imply that increase in the length of the alkyl side chain attached to the carboxylic group improves the miscibility of the fullerene derivative with the polymer P1. Butyl chains ($m = 4$) induce optimal degree of the phase separation between the components of the blend enabling balanced charge generation and charge transport required for efficient operation of photovoltaic cells. This hypothesis is supported by Fig. 14 which shows the dependence of the average lateral size of the clusters detected in the composite films by AFM and/or SEM as a function of the descriptor $m$.

The presented example illustrates that the molecular structure of the fullerene derivatives is a critical parameter which defines both the morphology and the photovoltaic performance of their composites with the polymer P1. The properties of these systems were correlated with a good accuracy with a structural descriptor $m$. The revealed correlation might be considered as the first step towards the development of a predictive model based on the material structure-composite morphology-photovoltaic performance relationships.
Fullerene derivatives with reduced electron affinity as n-type components for organic bulk heterojunction solar cells

There are many different conjugated polymers with very different optoelectronic properties which were designed for photovoltaic applications [114–116]. Almost all these materials were evaluated in solar cells in combination with standard materials such as [60]PCBM and [70]PCBM. However, the photovoltaic performance of many systems is limited by non-optimal alignment of the energy levels of the electron donor and electron acceptor components. This is a particular case of the [60]PCBM/P3HT blends which show rather low open circuit voltage of ~0.6 V due to very large (1.1 eV) energy offset between the LUMO of P3HT and LUMO of [60]PCBM. Optimal LUMO(donor) – LUMO (acceptor) offset was estimated to be in the range of 0.3 eV [117, 118].

It was also shown previously that providing appropriate acceptor material might improve $V_{OC}$ of the P3HT-based solar cells up to 1.2 V and double the solar cell efficiency [119]. Similar problem exists in many other polymer-PCBM systems. To solve this problem, some alternative acceptor materials with higher LUMO energies (which is equal to the lower electron affinity) are required (Fig. 15).

Typically, fullerene derivatives with reduced electron affinity are obtained via addition of the second organic addend (cyclic) on the fullerene cage as it is shown in Scheme 2. Fullerene derivatives with reduced electron affinity (higher LUMO energy) are required to decrease the energy gap between the LUMO(D) and LUMO (A) down to ~0.3 eV and improve $V_{OC}$ and overall power conversion efficiency of the solar cells.

Table 1: SEM and AFM images for the blends of fullerene F1, F7 and F9 derivatives with the polymer P1. Reproduced with permission from [93].

<table>
<thead>
<tr>
<th>System</th>
<th>SEM image</th>
<th>AFM image</th>
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<tbody>
<tr>
<td>F1+P1</td>
<td><img src="image1" alt="SEM image" /></td>
<td><img src="image2" alt="AFM image" /></td>
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<tr>
<td>$m=1$</td>
<td>$I_{sc}=2.3$ mA/cm², $\eta=0.9%$</td>
<td></td>
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<tr>
<td>F9+P1</td>
<td><img src="image3" alt="SEM image" /></td>
<td><img src="image4" alt="AFM image" /></td>
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<tr>
<td>$m=4$</td>
<td>$I_{sc}=8.3$ mA/cm², $\eta=3.9%$</td>
<td></td>
</tr>
<tr>
<td>F7+P1</td>
<td><img src="image5" alt="SEM image" /></td>
<td><img src="image6" alt="AFM image" /></td>
</tr>
<tr>
<td>$m=8$</td>
<td>$I_{sc}=5.3$ mA/cm², $\eta=0.9%$</td>
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Figure 13: Average lateral cluster size in the composites of F1-F12 with P1 plotted as a function of the structural descriptor $m$. Reproduced with permission from [93].
Figure 16: Influence of the positioning of the electron donor alkoxy group on the electronic properties of the fullerene core. Significantly reduced electron affinity of the ortho-substituted compound evidences the existence of through-space electron interactions between the lone electron pair of oxygen atom and the fullerene cage.

Scheme 2. The bis-cycloadducts (called bis-adducts below) are obtained as mixtures of many (8 to 25) isomers which can hardly be separated [120].

A number of bis-adducts demonstrated high solar cell efficiencies in combination with crystalline regioregular polymer P3HT [88, 121, 122]. However, replacement of P3HT with some alternative polymers typically results in very low device performances.

Theoretical modeling performed by Nelson et al. suggests an existence of a considerable energetic disorder in the mixtures of bis-PCBM isomers possessing somewhat different LUMO energies [123]. The energetic disorder is expected to lead to the charge trapping in the system reducing FF and $J_{SC}$ values of the devices. This conclusion was supported by experimental data reported by different groups [124, 125]. Disorder in the blends of the fullerene bis-adducts and low band gap conjugated copolymers is most probably responsible for their poor photovoltaic performance.

In order to avoid the formation of multicomponent isomer mixtures, many research groups pursued the design of fullerene monoadducts with reduced electron affinity. In this case the single organic addend was modified with electron donor groups (usually alkoxy groups RO-) in order to achieve the desired reduction of the electron affinity (increase of the LUMO energy). A number of very promising fullerene derivatives were synthesized [126–129]. However, they did not provide considerable improvement in the solar cell performance by now.

We have investigated systematically the effect of the introduced substituents on the electronic properties of the fullerene core. The obtained results can be illustrated by the row of fullerene derivatives with different positions of the electron donor alkoxy group in the phenyl ring (Fig. 16).

It is seen from the Fig. 16 that the influence of the electron donor RO group on the electronic properties of the fullerene cage increases in the row $\text{para} < \text{meta} < \text{ortho}$.

Some of these compounds have demonstrated good photovoltaic performances not just in combination with P3HT, but also in the blends with other conjugated copolymers such as PCDTBT. Fig. 18 shows that use of a properly designed fullerene derivative instead of PCBM improves both open circuit voltage and efficiency of organic bulk heterojunction solar cells [131].
Methanofullerenes bearing cyclopropane ring on the fullerene cage might be not the optimal compounds for realization of the through-space electronic interactions between organic addends and the fullerene cage. Pyrrolidinofullerenes discussed at the beginning of this review might be considered as better candidates since aryl substituents in the pyrrolidine ring are arranged in a close proximity to the fullerene cage. Some 1’,2’-disubstituted pyrrolidinofullerenes were investigated previously as promising materials for organic solar cells by K. Matsumoto et al. [97] We succeeded in the preparation of 1’,2’,5’-trisubstituted pyrrolidinofullerenes bearing two aryl groups in the pyrrolidine ring (Fig. 19) [132]. These compounds have demonstrated significantly lower electron affinities compared to [60]PCBM as it can be concluded from the cyclic voltammetry measurements (Fig. 20a). At the same time, they have demonstrated remarkably high open circuit voltages in photovoltaic cells. In particular, the devices based on the P3HT/PyF-4 blends have shown open circuit voltages of 778 mV (Fig. 20b). To the best of our knowledge, this represents the highest value achieved for fullerene monoadducts in combination with P3HT until now. It is also notable that PyF-4 provided even higher open circuit voltage than bis-PCBM according to the available literature data [88].

The presented results prove that rationally designed fullerene monoadducts represent very promising group of n-type semiconductor materials for efficient organic solar cells.

### 6 Novel electron donor conjugated polymers with tailored optoelectronic properties

As long as the efficiency of organic solar cells was dramatically improved, major concerns appeared regarding their stability [133–135]. Among hundreds of investigated polymers carbazole-TBT copolymer PCDTBT [136] (Fig. 21) has demonstrated an outstanding stability.

In particular, the lifetime of the PCBM/PCDTBT solar cells was estimated to be in the range of at least 6-8 years which is substantially longer compared to the P3HT/PCBM devices [137]. Nonetheless, optoelectronic properties of PCDTBT are not optimized with respect to PCBM used as electron acceptor counterpart because of a 0.55 eV LUMO-LUMO offset (Fig. 21). As a consequence, efficiency of organic solar cells based on this material combination can hardly exceed 7% [88, 138]. The reported reproducible
Experimental solar cell efficiencies for PCDTBT/[70]PCBM blends fall in the range of 5.6-6.6% [139–142]. The energy diagram for PCDTBT-PCBM system (Fig. 21) suggests that optoelectronic properties of the polymer can be improved by lowering its LUMO energy without affecting significantly the HOMO position. A number of previous attempts to modify the chemical structure of PCDTBT in order to lower its LUMO energy and/or reduce its band gap were unsuccessful and resulted in inferior solar cell performances [143–146]. Recently we have proposed an alternative approach for lowering the LUMO of PCDTBT and similar copolymers which is outlined schematically in Fig. 22 [147].

The PCDTBT repeating unit comprises in its molecular framework the electron deficient benzothiadiazole unit (acceptor “A”), two adjacent electron donor thiophene rings (donor “D”) and carbazole unit “X” which is considerably weaker electron donor compared to thiophene [148]. Therefore, PCDTBT represents an example of the (-X-DAD)$_n$ family of conjugated polymers. We proposed to introduce additional alternating A and D elements in the polymer repeating unit thus opening a pathway towards (-X-DADAD)$_n$ copolymers which are expected to have advanced optoelectronic properties as compared to the conventional (-X-DAD)$_n$ structures [149].

The application of this concept to PCDTBT leads to a novel polymer P2 comprising an extended TBTBT unit in its molecular structure. This polymer has been synthesized using chemical route illustrated in Scheme 3. Unfortunately, polymer P2 showed very low solubility in organic solvents due to the presence of a large planar TBTBT unit in its molecular framework. Therefore, it was not possible to obtain thin films of P2 suitable for fabrication of organic solar cells.

A family of highly soluble polymers P3-P7 comprising alkylthiophene units have been designed and investigated (Fig. 23) [150]. It should be emphasized that these polymers differ only by the attachment positions of the solubilizing alkyl side chains in the polymer backbone. However, positions of the alkyl side chains influenced dramatically optical, electronic and photovoltaic properties of polymers P3-P7.

Fig. 24a shows that polymer P7 has rather wide optical band gap which is even wider than that of PCDTBT. On the contrary, polymer P3 with a different arrangement of alkyl side chains demonstrates a narrow band gap of ca.
In general, the optical properties of this material are favorable for photovoltaic applications.

The solar cells based on polymers P3-P7 and [60]PCBM revealed drastically different performances. The highest efficiency of 5.1% was obtained for the polymer P3, while P7 showed the lowest efficiency of 0.6%. The obtained results suggested that polymer P3 might be considered as a promising material for organic bulk heterojunction solar cells. It is seen from the Fig. 25a that P3 has significantly lower band gap compared to PCDTBT. At the same time, the oxidation potentials of P3 and PCDTBT are almost the same thus suggesting that both polymers have very similar HOMO energy levels (Fig. 25b). The obtained results proved that using alternating DADAD building blocks instead of conventional DAD units indeed leads to the lowering the LUMO energies and reducing the band gaps of the resulting polymers.

The bulk heterojunction solar cells based on the composites of P3 with [70]PCBM have revealed appreciable power conversion efficiency of 6.4%. However, efficiencies of 9-10% are theoretically feasible for this system considering the opoelectronic properties of P3 and [70]PCBM (Fig. 26a). We believe that improved efficiencies can be reached soon via optimization of the material itself (e.g. molecular weight characteristics) and the photovoltaic device architecture.

Very important aspect is the operation stability of organic solar cells. It was mentioned above that the solar cells based on PCDTBT have excellent operation stability.

We proved that devices based on novel polymer P3 have comparable stability on the contrary to a number of reference systems based on other conjugated polymers such as PTB7, PBTTT-CF and etc. (Fig. 26b). It is reasonable to assume that advanced stability of the solar cells based on P3 is preserved since this material is constructed from the same photochemically inert building blocks as PCDTBT itself: thiophene, benzothiadiazole and carbazole.

The obtained results suggest that polymer P3 and other similar polymers can be considered as highly promising materials enabling high efficiency and long term stability of organic solar cells. In general, the proposed concept can be also applied to many other (X-DADAD)\(_n\) copolymers leading to more promising (X-DADAD)\(_n\) structures as it is illustrated in Fig. 27. The range of possible X units includes carbazole, fluorine, silafluorene, indolocarbazole, cyclopentadithiophene, dithienosilole, dithienopyrrole, benzodithiophene and etc. At the same time, benzothiadiazole can be equally replaced with other acceptor units such as benzooxadiazole, benzotriazole and quinoxaline. Further exploration of different (X-DADAD)\(_n\) systems is currently in progress in our labs.
7 Novel approaches for investigating stability of organic photoactive materials used in solar cells

It is known that even simple and robust non-conjugated polymers such as polypropylene, polystyrene or PMMA require special stabilizing additives to sustain simultaneous action of light, oxygen and moisture [151, 152]. Conjugated polymers are rather fragile substances and it is clear that they will require special protection in aggressive environment. Surprisingly, vast majority of publications on stability of conjugated polymers report results of aerobic tests [103–105]. It should be emphasized that different polymers might undergo very different degradation pathways in the reactions with oxygen and moisture. This could be reversible or irreversible doping of conjugated polymers, oxidation of their backbones or side chains, hydrolysis of some functions (e.g. amide in 1,4-diketopyrrolopyrrole units), cross-linking via [2+2] and [2+4] cycloaddition reactions and etc. [153–156] Most probably, organic solar cells can be applied practically only in combination with the appropriate barrier layers which can prevent (or at least diminish substantially) penetration of oxygen and moisture in the active layer of organic solar cells. However, the action of light and elevated temperatures cannot be avoided under the real solar cell operation conditions. Therefore, photochemical and thermal degradation of organic photoactive materials represent the most severe factors limiting durability of plastic solar cells. This is a reason why the investigation of photostability of conjugated polymers and fullerene/polymer blends under anaerobic conditions attracts more and more attention [123–159].

We proposed to apply ESR spectroscopy for monitoring photochemical and thermal degradation of different conjugated polymers in the absence of oxygen and moisture [160, 161]. The same technique has been also used recently by Leclerc group to study the accumulation of free radical species in the PCDTBT/PCBM blends under continuous illumination in the absence of oxygen and moisture [124]. More recently we have reported results of a comparative study of seven different conjugated polymers whose molecular structures are shown in Fig. 28 [162].

Our initial hypothesis was based on the assumption that some minor fraction of excitons generated in the polymer films under illumination undergo non-radiative quenching leading to the rupture of some chemical bonds and formation of novel species. Some of these species might represent stable radicals which could be detected by ESR spectroscopy. We have shown previously that such radical species behave as deep traps for mobile charge carriers and affect severely the performance of different conjugated polymers in organic solar cells [163, 164]. Therefore, continuous illumination of polymer samples is expected to result in accumulation of radical species and degradation of their photovoltaic properties.

The obtained results proved that conjugated polymers undergo degradation in the absence of oxygen and moisture under illumination with visible light resulting in gradual accumulation of free radical species. This behavior is clearly illustrated by exemplary sets of the ESR spectra obtained for conjugated polymer PTB7 (Fig. 29).

The sample of PTB7 contained initially very low concentrations of radical species. However, aging resulted in
the appearance of strong and unsymmetrical signals in the ESR spectra of the material thus suggesting simultaneous formation of few different radical species. Very similar results were also obtained for other conjugated polymers. Integration of the signals in the ESR spectra allowed us to reconstruct degradation profiles for each conjugated polymer (Fig. 30).

In order to compare the stability of the investigated conjugated polymers, we have analyzed their degradation profiles revealed using ESR spectroscopy (Fig. 30). It should be noted that concentrations of the radical species depend almost linearly on the aging time for all conjugated polymers in the time frame between ~100 and 1000-1300 h (Fig. 31a). The slopes of the linear fits presented in Fig. 31a define the initial rates of accumulation of radicals $\mathcal{R}_{\text{in}}$. Alternatively, one can also calculate average rates of accumulation of radicals $\mathcal{R}_{\text{av}}$ defined as $\mathcal{C}_{R}(\text{max})/T(\text{max})$, where $\mathcal{C}_{R}(\text{max})$ is a maximal concentration of radical species observed for a certain polymer, while $T(\text{max})$ is a time when this maximal concentration was reached.

Comparing the $\mathcal{R}_{\text{in}}$ and $\mathcal{R}_{\text{av}}$ values obtained for different conjugated polymers leads to very similar conclusions regarding the relative stability of these materials (Fig. 31b). It is reasonable to assume that the least stable materials are characterized by the highest $\mathcal{R}_{\text{in}}$ and $\mathcal{R}_{\text{av}}$ values and vice versa. The obtained experimental results strongly suggest that P3HT and, especially, PCDTBT are the most stable conjugated polymers. On the contrary, PTB1, PTB7 and PBDTTT-CF comprising thieno3,4-bithiophene units in their molecular frameworks demonstrated the lowest stability (Fig. 32).

Thus, the ESR spectroscopy was shown to be very useful technique for monitoring photochemical and thermal degradation and comparing the stability of different materials designed for photovoltaic applications. The experimental results reported in [128] imply that light is the most crucial factor inducing the degradation of polymers PCDTBT, SiPCPDDBTBT, F8TBT and P3HT, while heat along leads to very minor effect (F8TBT) or has no influence at all (PCDTBT, SiPCPDDBTBT). On the contrary, thermal degradation of polymers PTB1 and PBDTTT-CF proceeds with comparable rates to photochemical degradation.

Conjugated polymers comprising thieno[3,4-b]thiophene units (PTBT1, PTB7, PBDTTT-CF, PBDTTT-CT, and etc.) are extensively studied nowadays by many research groups around the world as promising electron donor materials providing high efficiencies (7-9%) in organic solar cells [165, 166]. However, the results presented in [128] strongly suggest that this type of materials can hardly find any practical applications due to their inferior thermal and photochemical stability. More stable materials resembling the behavior of conjugated copolymer PCDTBT (and also P3HT to some extent) have to be designed to meet long-term stability criteria required for real outdoor implementation of organic photovoltaics.

**Summary and outlook**

Approximately fifty years ago Soviet scientists at the Institute of Chemical Physics in Chernogolovka (currently IPCP RAS) constructed their first organic solar cells based on phthalocyanines as light absorbing materials [16–19, 22–23]. They were among the first (or even very first) researchers who observed unusually efficient exciton splitting at organic p/n junctions resulting in generation of mobile charge carriers with the quantum yields close to 100% [19, 21, 22]. The first designed organic photovoltaic cells comprising p/n junctions induced by doping of organic semiconductors with appropriate species were not very efficient ($\eta$~0.1-0.5%). However, the concept itself was intensively developed since groundbreaking report of C. Tang demonstrating efficient bilayer p/n junction devices [24]. Nowadays, organic photovoltaics represents a prominent research field developed by many groups worldwide.

The presented report provided a brief overview of the research activities in the field of organic photovoltaics at...
the Institute for Problems of Chemical Physics of Russian Academy of Sciences in Chernogolovka (IPCP RAS) during the last decade. Nowadays more or less any kind of scientific research has a clear interdisciplinary character. Therefore, virtually all given above examples and the presented results were obtained in the frame of successful collaborations of IPCP RAS with a number of Russian and International partners.

Outside the scope of this review we left activities of our group (again together with collaboration partners) at IPCP RAS in the field of light emitting diodes [167–172], biocompatible and biodegradable electronics [174–177], field-effect transistors [178], photodetectors [179–181] and memory elements [182].

We believe that the present review and the entire topical issue “Organic Photonics and Photovoltaics in Russia” will catalyze novel multinational collaboration research projects involving Russian teams working in the field of organic electronics.

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