

# Alternating Polyfluorenes Collect Solar Light in Polymer Photovoltaics

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## **CON SPECTUS**

The effort to improve the energy conversion efficiency of polymer solar cells has led to the design of novel donor polymers. To improve open circuit photovoltages (OCVs) and the spectral coverage of the solar spectrum, researchers have looked for materials with high HOMO values, an easily modified electronic structure, and sufficient electronic transport within the polymers. One advance in design from our laboratories has been the development of a class of alternating polyfluorene copolymers (APFOs), which can be combined with fullerenes to make bulk heterojunction materials for photovoltaic conversion.

This Account describes copolymers of fluorene that we designed to expand the range the optical absorption of solar cells to include wavelengths out to 1000 nm. In most cases, we



combine these polymers with acceptors from the fullerene family, typically the phenyl  $C_{61}$  butyric acid methyl ester (PCBM) molecule, to generate solar cell materials. The synthesis of alternating copolymers of fluorene with various donor—acceptor—donor elements provides the opportunity to shift both HOMO and LUMO, which we have followed by electrochemical spectroscopy. Moving the LUMO of the APFOs farther from the vacuum level eventually leads to a situation where the driving force for photo-induced charge transfer from polymer donor to fullerene acceptor goes to zero, resulting in inefficient charge generation. Moving the HOMO level closer to the vacuum level reduces the OCV of devices made from bulk heterojunction blends. As we move the bandgap toward lower energies and increase the overlap of optical absorption with the solar spectrum, both these events eventually occur.

In devices based on these APFO/fullerene blends, the performance depends on the OCV, the photocurrent under solar illumination, and the fill factor. The fill factor is influenced by electrical transport and charge generation. Optimizing these parameters requires new solutions to the perennial conflict between optically thin devices, where electrical extraction of charge is not a limitation, and the optically thick devices, where extraction of charge is hampered by trapping and recombination. As a result, we have developed methods to trap light in optically thin devices. When the thin film flexible solar cells are folded, multiple reflection between adjacent solar cells leads to a longer path length for the photon through the devices and considerable improvement of the optical dissipation in the active material. These optical tricks also enable an alternative route to tandem devices, where two different bandgap materials are located on adjacent folds. Thus light not absorbed in one cell is reflected onto the next cell to produce an effective optical series arrangement. Using experiments and simulations of the light trapping effects, we demonstrate power conversion efficiency enhancements of up to a factor of 1.8.



**FIGURE 1.** Generic structure of alternating polyfluorene copolymers and device data; external quantum efficiency of four different APFO/ fullerene combinations, demonstrating coverage of a major part of the solar spectrum.<sup>2–5</sup>

#### 1. Introduction

The current expansion of research in organic solid-state photovoltaic materials and devices,<sup>1</sup> now moving into technical development and first use, is fueled by the growing number of conjugated polymers and molecules serving as optical absorbers in the visible range of radiation and eventually as media for transport of photogenerated charges. There is a need to introduce solutions to the major problems of present day devices already at the materials design phase. Dominant materials today are the combinations of poly(3-hexylthiophene) with a soluble methanofullerene derivative. The low open circuit photovoltage (OCV) and the narrow spectral coverage are limiting factors, while the transport properties are adequate for optically thick devices. Still, the major loss of voltage, from photons of blue and green colors above 2 eV, to the device voltage of 0.6 V is very large and is a limiting property for an otherwise highly performing material. There is a need for new materials to better use the free energy of the photon in extracting electrical energy. There is also a need to extend the solar spectrum coverage to reach higher photocurrents.

In this Account, we describe a class of conjugated polymers, copolymers of fluorene with donor-acceptor-donor (DAD) segments to modify the optical absorption, to cover the solar spectrum out to 1000 nm (Figure 1). The polymers can be combined with acceptors from the fullerene family, mostly the phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) molecule, to generate solar cell materials. As we vary optical properties of the polymers, we also shift the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) positions. Therefore we need to match the changing donor LUMO with the appropriate acceptor LUMO. The tuning of conditions for photoinduced charge transfer requires variation of acceptor molecules, and we have used a number of substituted  $C_{60}$  and  $C_{70}$  derivatives, giving a small span of redox potentials. Where conditions for charge generation and optical absorption have been obtained, we need to make sure that

electrical transport is sufficiently efficient to compete with back reactions in the form of recombination. Sufficient optical input into the device must be done within a thickness low enough that photogenerated charges can be electrically collected.

# 2. Chemical and Electronic Structure of Alternating Polyfluorene Copolymers (APFOs)

The synthesis of soluble polyfluorenes was first reported by Yoshino<sup>6</sup> and Pei,<sup>7</sup> and this class of polymers<sup>8,9</sup> has been the basis for extensive development of polymers for light-emitting diodes,<sup>10,11</sup> lasers,<sup>12–14</sup> transistors,<sup>15</sup> and photovoltaic devices.<sup>16,17</sup> Copolymers of fluorenes were rapidly introduced for all these applications, and we have focused on development of polymers for photovoltaic devices. All APFOs are alternating copolymers, where the fluorene is alternating with a DAD segment (Figure 1).

**2.1. Chemical Structures and Synthesis of APFO Polymers.** In the design of the alternating polyfluorene copolymers, we use solubilizing fluorene units between the low band gap donor–acceptor–donor (DAD) segments. The donor is typically a thiophene unit, and the acceptor varies from benzothiadiazole to more electron-withdrawing units. Most of the DAD structures in the APFOs have been described earlier.<sup>18</sup> The low band gap is achieved by a partial charge transfer within the DAD unit resulting in red-shifted absorption and a lower bandgap.<sup>19</sup> Structures of some APFOs are described in Figure 2, and the action spectra of several polymers, combined with fullerenes, in solar cells can be seen in Figure 1.

In Scheme 1 the synthesis of the simplest APFO polymer, called APFO-3, is described. This polymer is synthesized according to the procedure in our first report about these polymers.<sup>20</sup> The polymer has a relatively high band gap (1.9 eV), due to the use of the relatively weak electron-accepting unit. To achieve solubility in all of the described polymers, straight octyl side chains are used on the fluorene unit. All polymers are synthesized using palladium-catalyzed Suzuki polymeri-



FIGURE 2. Structures of some APFOs.

zation reactions, coupling the dibromides of the DAD segments together with the diboronic esters of the fluorene units. To reach high molecular weight, it is important to use a stoichiometric ratio of the two comonomers. However, to increase the yield of soluble polymers in some cases, nonstoichiometric ratios have been used to deliberately decrease the molecular weight. Molecular weights of the polymers are presented in Table 1.

By use of other electron-accepting units, polymers with lower band gap have been synthesized. Replacing the benzothiadiazole with a thieno[3,4-*b*]pyrazine results in APFO-Green-2<sup>21</sup> and APFO-Green-5,<sup>3</sup> both with a bandgap of 1.5 eV, which are labeled "Green" because they are green in their neutral state. In the synthesis of these polymers, we have lately chosen to brominate the DAD segment at an earlier stage in the synthesis of the monomer to avoid the risk of overbromination,<sup>22</sup> which can occur if the bromination is done as the last step of the monomer synthesis. To increase the molecular weight of the chloroform soluble fraction of the polymers, side chains were added onto the DAD segment in APFO-Green-5. This resulted in a polymer with higher molecular weight.

In the synthesis of APFO-Green-9<sup>4</sup> and APFO-Green-1,<sup>23</sup> the same starting material is used (Scheme 1). Reducing this compound under different reaction conditions can form a tetraamine or a diamine intermediate. Condensing these with benzile gives two different DAD segments. From the tetraamine pyrazino[2,3-g]quinoxaline is formed, and after bromination, this monomer is used to synthesize APFO-Green-9.

**SCHEME 1.** Synthetic Route to APFO Polymers APFO-3, APFO-Green-2, APFO-Green-5, APFO-Green-9, and APFO-Green-1



TABLE 1. Molecular Weights of Some APFO Polymers<sup>a</sup>

polymer	Mn	M <sub>w</sub>	PDI
APFO-3	4900	11800	2.4
APFO-Green-2	8600	22000	2.6
APFO-Green-5	40000	95000	2.4
APFO-Green-9	13000	30000	2.3
APFO-Green-1	3600	6200	1.7

<sup>*a*</sup> Molecular weights and polydispersity index determined by size-exclusion chromatography (SEC) using polystyrene standards and 1,2,4-trichlorobenzene (135 °C) as solvent.

The strength of the acceptor unit in this polymer is stronger than the previously described acceptors, resulting in a polymer with a bandgap of 1.4 eV. An even stronger acceptor is formed if only the diamine is used, thus forming a thiadia-zolo[3,4-*g*]quinoxaline unit. This unit is used in APFO-Green-1 where the bandgap is 1.3 eV, the lowest in this series.



FIGURE 3. Location of bandgap and band edges of HOMO and LUMO (vs vacuum) of APFOs. Data obtained from peak potentials in SWCV.

**2.2. Electronic Structure.** The electronic structure of APFOs is partially accessible through photoelectron spectroscopy and electrochemical spectroscopy, in which one or both of the HOMO or LUMO can be obtained. The location of the orbitals is critical to obtain conditions suitable for charge transfer and for determining the OCV in blend materials with acceptors.

**2.2.1. Electronic Structure through Electrochemistry.** A preferred method to study the electronic structure of polymer donor and acceptors is electrochemical spectroscopy. Here charge injection is used to probe the position of the HOMO and LUMO states in redox-active compounds. We have used cyclic voltammetry (CV) and square wave voltammetry (SWCV) to determine energy levels of polymer donors and molecular acceptors. With many caveats, we can construct the map of HOMO and LUMO orbitals of the polymers,<sup>5,24,25</sup> presented in Figure 3.

2.2.2. Electronic Structure through Optical Absorption and Emission. An alternate and important route to characterize these polymers is through their optical processes of absorption and emission, probing transitions between the electronic states of the polymer. Because the optical absorption is the most crucial element when building photovoltaic materials, this property is the first to be used, but the subsequent track of optical excitations moving through the polymer is of considerable interest, because this is the route to charge generation. Quantum chemical modeling of neat APFO-3<sup>26</sup> has been done, using semiempirical Zerner's intermediate neglect of differential overlap (ZINDO), revealing that the low-energy absorption peak found in this polymer is due to a charge transfer band localized on and associated with the DAD segment, and the high-energy absorption is due to a more delocalized state. An important observation is that the localization

is in the LUMO and that the HOMO is delocalized, which is in line with the electrical properties, which reveal only very poor electron mobilities while hole mobilities are decent.

The steady-state absorption and emission spectra are therefore due to these states; excitation spectra can be affected also by dark intermediate energy states. Transient photophysical studies of the same polymer<sup>27</sup> further contribute to the description of the transport and reactions of excitons in the neat polymer. Generation of charges is feasible in the neat polymer, with a low yield,<sup>28</sup> through singlet exciton dissociation but also through exciton-exciton fusion and subsequent reactions. The delayed fluorescence observed in this polymer is due to polaron pair recombination on the longer time scale.<sup>26</sup> In APFO-Green polymers designed for extended absorption into the near-infrared range, semiempirical ZINDO calculations once more contribute well, to the point that predictions of optical oscillator energies and amplitudes from the quantum chemical modeling can be used to fit the experimentally observed dielectric function of the polymers APFO-Green-1 and APFO-Green-2.<sup>29</sup> The low-energy absorption peaks in these two polymers are also localized at the DAD comonomer.

**2.3. Photophysics of APFO/Fullerene Blends.** Very detailed studies of the transient optical absorption spectra of APFO-3/PCBM blends have been performed.<sup>30</sup> The generation and decay of excited states and charged polaron states, after a femtosecond light pulse, have been followed over 9 orders of magnitude in time, ranging from 30 fs to 50  $\mu$ s time. From use of different donor/acceptor stoichiometries and light intensities, a comprehensive picture has emerged. This has resulted in a full reaction kinetic model of the dynamics of photogenerated excitations in the film. Summarized, the model describes the excitation (and bleaching of the transi-



**FIGURE 4.** Morphology of blend APFO3/PCBM film with weight ratio of 1:4 spin-coated from chloroform solution: (left) top surface by scanning force microscopy: (right) 3D nanostructure by electron tomography<sup>36</sup> The contrast in the tomography image is due to electron scattering, which is higher in PCBM.

tion), the formation of a bound polaron pair, and the subsequent geminate recombination of this polaron pair, with a lifetime of ~30 ns. This is the dominating route at low light intensity, which corresponds to solar cell illumination conditions, while there are other routes available at higher illumination levels. The nongeminate recombination is of little importance in these studies. A conclusion is also that the generation of photoinduced charge carriers, detected through the suppression of photoluminescence, is almost complete already at very low acceptor concentration<sup>28</sup> and therefore that there is an acceptor close to all polymer chains in the APFO-3/PCBM system.

The photophysics also indicate a close to 100% efficiency of charge transfer from polymer to fullerene, and since only one recombination process that can clearly be outcompeted by transport is relevant, it is thus reasonable to conclude that given a suitable morphology and sample geometry, almost all photogenerated carriers should be possible to extract.

2.4. Morphology in Blends and Pure Polymers. In our studies of the nano- and microstructure of polymers and polymer blends with acceptors, we have used scanning force microscopy (SFM) at the submicrometer range and optical microscopy above the micrometer range. The SFM method is limited to studies of the surfaces of the sample, while the optical method can allow probing of the full volume of the material but at very coarse resolution. Though the resolution of the SFM method is not quite up to the required 5-10 nm matching the diffusion length of the exciton, there is always the caveat that only the surface is imaged in SFM. Because photoelectron spectroscopy reveals that the dominant material on the top surface in APFO-3/PCBM blends is the polymer,<sup>31</sup> we must be wary to interpret the images obtained from SFM. Nevertheless, we have coupled the imaging to processing issues, preparing bulk heterojunction materials from different solvent environments, and correlated the device performance to the nanostructure. The morphology of a binary system can be influenced by adding small amounts of a different solvent (1-2%) with low evaporation rate into a solvent with fast evaporation.<sup>32</sup> There is then a continuous shift of the solvent composition as the solutions dry out during spin coating to make a solid film. The resulting nanostructure can be quite different, as demonstrated for the addition of toluene or chlorobenzene to chloroform solutions.<sup>32</sup> As now evident in many more studies of cosolvents and additives during film formation, the competition between solvation and precipation in polymer and acceptor molecule rule the formation of nanostructure.<sup>33,34</sup> The resulting structures are generally not in thermodynamic equilibrium, and therefore annealing by thermal excursions or solvent exposure lead to geometrical change.

The use of secondary ion mass spectroscopy (SIMS), using an ion beam to ablate the sample and recording the mass spectra of departing materials, makes it possible to image the vertical organization of the bulk heterojunction materials.<sup>35</sup> From these studies, which average the lateral distribution of chemical species but allow imaging of the stratification through the film, it is clear that very complex geometries are possible. A multilayer is recorded, where the polymer and PCBM concentration vary in more than one wave. To reconcile these different imaging results, which are different but internally consistent, for instance, in both XPS/UPS<sup>31</sup> and SIMS<sup>35</sup> a polymer enriched phase is found on top of the sample, we need a tool to record the three-dimensional nanostructure of the polymer/molecule blend.

We have recently used a three-dimensional reconstruction method to image the full nanostructure of a bulk heterojunction material, through electron tomography.<sup>36</sup> Here electron scattering is recorded from the thin film sample in transmission geometry, and the angle of incidence of the incoming electron beam is varied over a wide span. The scattering images can be used to reconstruct the scattering object using tomographical methods. The graphical reproduction of these images (Figure 4) in no way does justice to the wealth of information obtained when viewing small video sequences obtained by sectioning the tomographical representation of the samples and scanning through the thin film sample. The strong contrast ratio (~3) of electron scattering found between polymer and PCBM allows us to identify the most scattering phase with PCBM-enriched domains but does not prove that no polymer is present in this domain. Electron tomography is a very promising technique to evaluate the morphology of blends.

# **3. Electrical Transport in Polymers and in Blends**

Electrical transport properties of the active materials found in polymer photovoltaics have been studied by both steady-state and transient electrical methods. They include studies of diodes, of varying thickness and temperature, where fitting of the space charge limited currents at higher voltages to models of transport in disordered solids allow determination of a steady-state mobility and the field dependence of this mobility. The model of Bässler<sup>37</sup> and Blom<sup>38</sup> has been used in these simulated current-voltage characteristics, and they have been used to build an understanding of the electron and hole mobility in polymer/acceptor blend of different polymers and acceptors. It was observed that addition of PCBM to APFO polymers would always enhance the hole mobility, but that some alternate fullerene acceptors would degrade the hole mobility.<sup>39</sup> With use of field effect transistors (FET), similar lessons were learned, but also in cases where both the hole and electron mobility could be observed in the FET measurement, the hole mobility would typically be higher.<sup>40</sup> This can be understood as a reason for the necessity of using large amounts of PCBM in blends. To obtain a better balance of charge transport for holes and electrons, 80% PCBM is necessary, while it is not at all necessary from the point of view of charge generation.<sup>28</sup> The FET measurements are inherently difficult, because considerable hysteresis is found in the behavior, possibly a fundamental aspect due to the disorder in the materials.<sup>41</sup> Both intrinsic and extrinsic factors contribute to these hysteresis phenomena.<sup>42</sup> Because transport measurements in FETs and in diodes are different, probing different directions of transport as well as different densities of charge, it is advantageous to use solar cells in these measurements and to operate them at conditions and geometries relevant to solar cells. It has in some cases been possible to



**FIGURE 5.** (a) Photocurrent (mA/cm<sup>2</sup>), (b) fill factor, (c) power conversion efficiency (%), and (d) CELIV electron ( $\times$ ) and FET hole (**■**) mobility (in cm<sup>2</sup>/(V s)) at varying stoichiometry APFO-3/PCBM, and correlation to device performance.<sup>44</sup>

observe both electrons and holes in charge extraction in linearly increasing voltage (CELIV) measurements of solar cells (based on APFO-Green-5) further corroborating the assignment of mobilities.<sup>43</sup> The correlation of stoichiometry, mobility and performance in APFO-3/PCBM solar cells has been further highlighted in FET studies (see Figure 5).<sup>44</sup>

### 4. Device Engineering

The materials created by mixing APFO and fullerenes are interlaced between two electrodes, at least one of which is transparent. Optical input into the active layer is influenced by the transmission and reflection of electrodes throughout the layers and at the interfaces between substrate, electrodes, and the active layer. Making the best use of solar light is critical to obtain high photocurrents; choosing the proper electrodes and interfacial layers is critical to generate high OCVs and fill factors.

**4.1. Open Circuit Photovoltages and Interface Engineering.** The high OCVs  $(1-1.1 V)^{20,45}$  found in devices from some APFO/PCBM blends compare favorably to the 0.6 V obtained in devices of poly(3-hexylthiophene) (P3HT)/PCBM, where the edge of optical absorption is quite similar. When extending the absorption to higher wavelengths in APFO-Green materials,<sup>5</sup> we reduce the OCV and may also require alternative acceptors.<sup>46,47</sup> The best combination can give 0.8 V at 900 nm excitation.<sup>4</sup>

For one and the same bulk heterojunction material, OCVs may vary depending on the nanostructure<sup>32</sup> and electrodes with buffer layers.<sup>48–50</sup> The model proposed by Ramsdale<sup>17</sup> indicates that the combination of Fermi level splitting at the heterojunction and diffusion potentials at the donor and acceptor phase cause a combined OCV, where also the injection of charges from the anode and cathode assist. This is fully consistent with the observations that modifications of buffer materials, which result in varying dark injection currents, also



FIGURE 6. Fully flexible solar cells with polymer anode: (a) geometrical structure; (b) flexibility,<sup>52</sup> (c) ITO-free anodes<sup>53</sup> for flexible solar cells.

influence the OCVs obtained. In devices that rely on aluminum cathodes deposited by evaporation, we regularly include a very thin layer of LiF, deposited by evaporation, enhancing the OCV.<sup>31,51</sup> An alternative approach is to deposit a submonolayer of poly(ethylene oxide) (PEO) from solution, on top of the active layer and before evaporation of the aluminum cathode.<sup>51</sup> In an alternative inverted geometry, which can be produced without use of vacuum, the cathode is created by a thin submonolayer of PEO on top of indium tin oxide (ITO), which moves the work function to low levels.<sup>50</sup>

On the anode side, injection of holes should be suppressed to obtain a high OCV. It has been demonstrated that various forms of the ubiquitous poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT(PSS)) buffer layer will contribute to different OCVs (and photocurrents).<sup>48,49</sup> In recent times, we have found that fully flexible polymer anodes are best assembled by making a bilayer of a very high conductivity PEDOT(PSS) and a lower conductivity PEDOT(PSS), which is in immediate contact with the active material.<sup>52</sup> With this construction, we obtain lower surface resistance but retain the beneficial properties of the PEDOT(PSS) contact, where considerable enrichment of the PSS phase is found.

We have substituted the standard ITO layer with a current collector in the form of a Ag grid and a coating of a highly conducting PEDOT(PSS).<sup>53</sup> Here we deposit the metal grid by use of a soft lithographic method. The loss of photocurrent through shadowing from the metal grid is compensated by the reduced electrical loss due to power dissipation in the transparent anode, and we find the trade-off to appear at ~5% coverage of the area with metal grid. In addition, we find from optical simulations that a large amount of solar energy is dissipated inside the ITO layer. In fact, we see a small increase of photocurrent when we substitute the ITO with the current collector. The major advantage of this substitution is however found in cost and flexibility (Figure 6). The cost of ITO is too high for photovoltaic uses, and ITO on plastics will easily crack



**FIGURE 7.** Folded solar cells in tandem configuration allow extended spectral coverage with more than one material, and electrical parallel or serial connections of individual absorber elements.<sup>56</sup>

during bending, and is therefore difficult to use in large area roll-to-roll production.

4.2. Light Incoupling for Maximizing Power Conversion Efficiency. The conflict between electrical and optical properties of organic semiconductors in solar cells calls for many remedies. For thick films, poor electrical transport, rapid recombination, and trapping of photogenerated charges may reduce the collected photocurrent; the increase of distance for charge transport and the decrease of internal electric field put a severe penalty on thick devices. For thin films, optical absorption may not be enough to collect incoming sunlight. We have developed three major approaches to enhance light incoupling into thin organic layers: plasmon assisted incoupling,<sup>54</sup> microlenses,<sup>55</sup> and folded reflective solar cells,<sup>56</sup> with structuring on the 100 nm level, the 10–100  $\mu$ m level, and the 10–10000  $\mu$ m level. The complexity of the physics goes from advanced to trivial, and the trivial is the most rewarding, since almost doubling of light incoupling can be accomplished. With folded solar cells (Figure 7),<sup>56-58</sup> in which light is repeatedly reflected between solar cells in a fold, we can trap light and improve optical coupling into thin films to enhance the power conversion efficiency (PCE). We can connect the individual solar cells in series or in parallel, gaining 1.7-1.8-fold improvement of the efficiency. By using different polymers on the two sides, we can make tandem solar cells, extending the solar spectrum coverage while reducing the loss of free energy on photovoltaic conversion. Simulations verify that for very thin film solar cells, doubling of the PCE is feasible, but losses in electrodes are severe.<sup>59,60</sup>

#### 4. Conclusions

The class of APFOs has been developed over 2002–2008 with the goal to arrive at suitable polymers for combinations with fullerenes, to obtain higher OCV and PCE, and to extract more photocurrent from the solar illumination. The solar spectrum is covered, and candidates for tandem solar cells exist. In the single materials cells, with record PCE of 3.5% in our lab and 4.2% at ECN,<sup>61</sup> they are certainly interesting candidates, and further development is expected to enable higher efficiency. Light trapping with folded cells affords an easy solution to the conflict between optical absorption and electrical transport, but energy dissipation in electrodes still limits the performance of devices.

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**Mats R. Andersson** was born in Kungälv, Sweden, in 1966, received his Ph.D. in Chemistry at Chalmers University of Technology in 1995, and completed a postdoctoral fellowship at University of California at Santa Barbara. Since 1996, he has been research associate at Chalmers University of Technology and was appointed Full Professor in Polymer Chemistry in 2008. His main research interests concern design and synthesis of new materials for polymer electronics.

#### FOOTNOTES

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