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Photoelectroactive modifying fullerenes.

Modifying fullerenes combined with high conducting polymers may contribute to the development of improved electronic and optoelectronic devices. This article view work on highly functional and processable polyaniline fullerenes composite materials. It demonstrates the close relation between functionality and processing behaviour and describes fullerenes-polymer interaction.

Key Words: fullerenes, organic photovoltaic, solar cell, polyaniline, phthalocyanine.

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Light can be considered an energy source which is capable of remotely switching functionality compound, effecting structural and chemical transformations of molecules. Today, two classes of materials are of paramount interest in the field of research into the optoelectronic applications of organic electronics: electroactive polymers and carbon materials. Energy management, storage and redistribution are important considerations in natural and modifical molecular architectures and light harvesting elements which can be controlled with high precision. Reversible energy transfer processes are being harnessed in this regard with to incorporation in modifying fullerenes. Photochemical changes are equally being used to modulate different properties such as host-guest interactions or electronic properties [1, 2, 5].

Electroactive polymers it polymers that possess the electrical, electronic, magnetic and optical properties of a metal and the mechanical properties of a conventional polymer. In the doped state, the backbone conducting polymer consists of a truly conjugated and delocalized *p*-electron system that provides semiconducting, conducting and other electroactive properties. Doping may be carried out chemically or electrochemically and always involves doping counter ions which stabilize the doped state. Their properties are intrinsic to “doped” forms of polymers [1, 3, 9].

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Фотоелектроактивація модифікованих фуллеренів.

Модифіковані фулерени в поєднанні з провідними полімерами можуть сприяти розробці більш досконалих електронних та оптоелектронних пристроїв. Ця робота оглядає функціоналізацію та трансформацію поліанілін – фулерен композитних матеріалів. Це свідчить про тісний зв'язок між функціональністю, процесом обробки та описує фулерен-полімерну взаємодію.

Ключові слова: фулерен, органічний фотоелемент, сонячна батарея, поліанілін, фталоціанін.

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The non-redox doping process in polyaniline, using photonics acids modifying fullerenes non be polymerized. During this doping process the number of electrons associated with the polymer backbone does not change. However, the energy levels are rearranged and a stable 2-D polychanges radical cation is produced, leading the polymer into a highly conducting regime. The highly conducting form of polyaniline, which corresponds to a oxidante, can be reversibly dedoped into its non-conducting base form. Moreover, the whole process is accompanied by very beautiful and reversible changes. Some other typical intrinsically conducting polymers are polypyrrole, terthiophene and poly-3,4 ethylenedioxythiophene is illustrated in Figure 1.

The key to further progress lies in improving

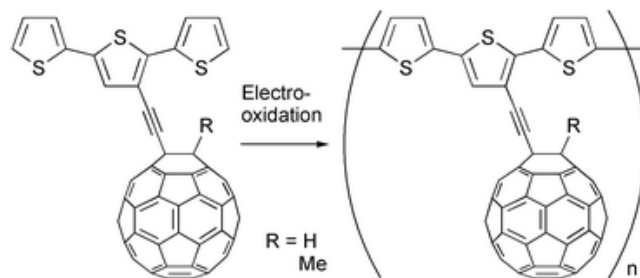


Fig. 1. Synthesis systems fullerene – terthiophene dyads for to create electroactive polymer films. Electropolymerization modifying fullerenes with metallized oxidate by radicals. [1].

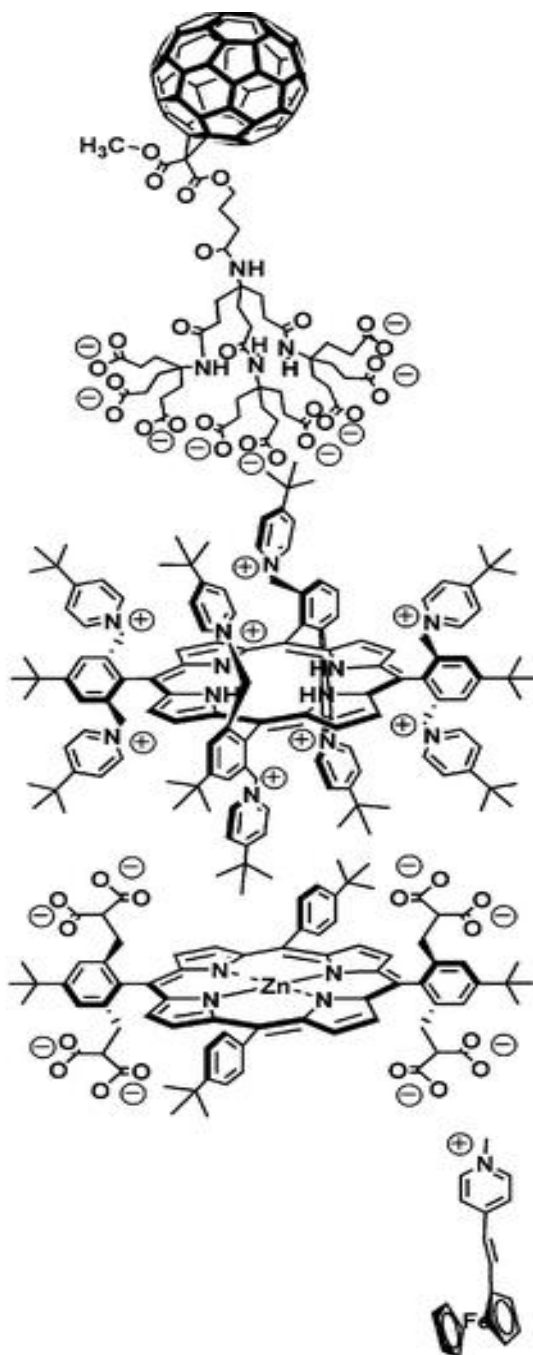


Fig. 2. Photoelectrochemical cell incorporating electrostatically interacting fullerenes, porphyrins and ferrocenes for solar cell that give rise to energy and redox gradients. [1, 7].

charge carrier mobility and processing. Systems fullerenes - porphyrins can be successfully used as integrative components in multifunctional hybrid cells that reveal considerable promise for applications as photochemical energy conversion systems is illustrated in Figure 2. Modifying fullerenes can be also considered natural partners for intrinsically conducting polymers. Their dimensions and electronic structure combine well with the chain

structure and the delocalized electron system of these electroactive polymers. Their mutual interactions may lead to highly favourable synergetic effects between both constituents, which might contribute to further improvements in organic electronic devices.

With these considerations in mind novel composite materials, based on modifying fullerenes and electroactive polymers been researched. I focused on two key issues: enhanced functionality and the processing properties of the obtained materials. These issues are directly linked to favourable interactions between the modifying fullerenes and the polymer chains. Thus, they are also closely related to the synthesis approach and self-assembling processes. I will outline this approach in the following description of our research on polyaniline - modifying fullerenes composites [4].

Directly after synthesis, I took a *UV-Vis* spectrum of fullerenes and modifying fullerenes solutions (Figure 3). The maximum at 330 nm corresponded to the $p-p^*$ transition centred on the benzenoid unit of fullerenes. The maximum at 475 nm corresponded to the quinoid exciton band. However, it was striking that the modifying fullerenes solution showed a new and very strong band with its maximum at 323 nm. This band was related to the $p-p^*$ transition centred on the quinoid unit. It would seem that the presence of fullerenes led to the enhanced response of the related rings. The rest of the features were identical to pure fullerenes. This led to view that this is a two-phase system: free fullerenes, and a new phase of fullerenes whose conformation is more size, a fact that is related to the presence of fullerenes [4, 8].

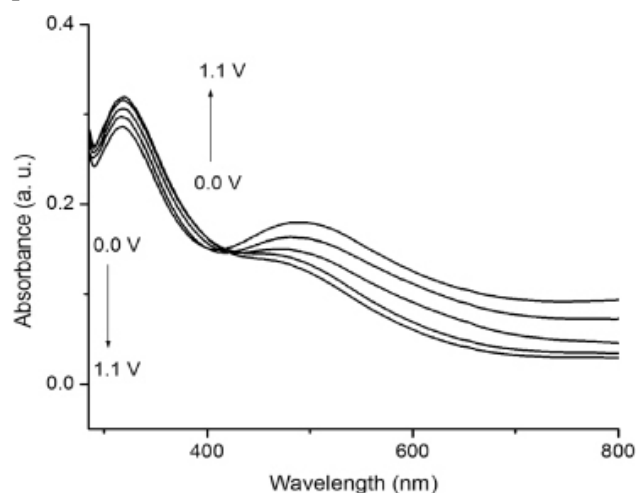


Fig. 3. *UV-Vis* absorption spectra in polyaniline - C_{60} after electrolysis. Modifying fullerenes (curves from top to bottom) after processes electrolysis performed: under inert atmosphere, air, gel, aqueous solution, salt solution for the range 280=800 nm [2].

As a next step, I tested the functionality of the material. First, performed temperature - dependent conductivity measurements on the bulk powder materials. The room temperature value for fullerenes fell below the experimental limit (below 10^{-10} S/cm). Therefore, no temperature dependence could be measured (Figure 4, 5). However, with about 0,1 S/cm, the room temperature conductivity for the modifying fullerenes powder drastically increased by at least nine orders of magnitude compared to fullerenes. Its temperature dependence resembled that of the fullerenes, indicating that conduction occurred through a percolated three-dimensional network of fullerenes. However, the room temperature value of the modifying fullerenes composite did not reach the value of a fullerenes network, which is expected to be one or two orders higher in magnitude. This indicates the existence of additional tunnelling barriers between the fullerenes, formed by the coating around the fullerenes. As a further indication of functionality, I observed the enhanced thermal stability of the composite, which decomposes in air at temperatures 120 °C higher. Secondly, I investigated the photophysical properties of the composite and measured its photoluminescent behavior ($\lambda_{exc} = 330$ nm) [4, 6] (shows, Figure 3). Shows that's a broad emission maximum modifying fullerenes at about 410 nm caused by reduced benzenoid/amine groups.

Self-assembled monolayers of fullerene-porphyrin systems, is the most frequently and systematically studied approach for the construction of nanostructured photoelectrodes. In particular, covalently linked dyad and triad conjugates involving porphyrins and fullerenes with a thiol functionality have been self assembled onto gold electrodes for photocurrent measurements is

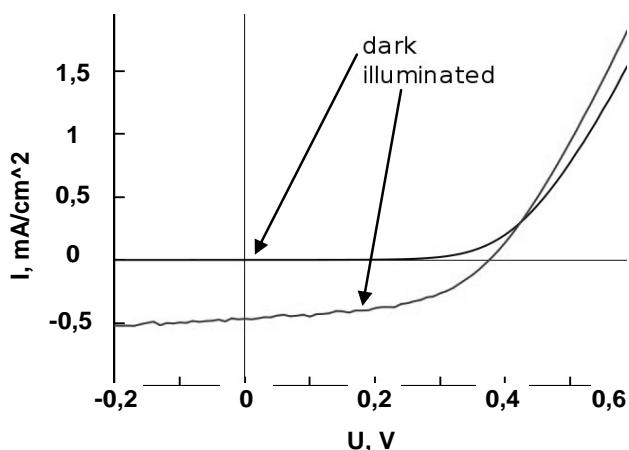


Fig. 4. *I-V* characteristics of inverted polyaniline - C_{60} bulk-heterojunction solar cells with and without light modification.

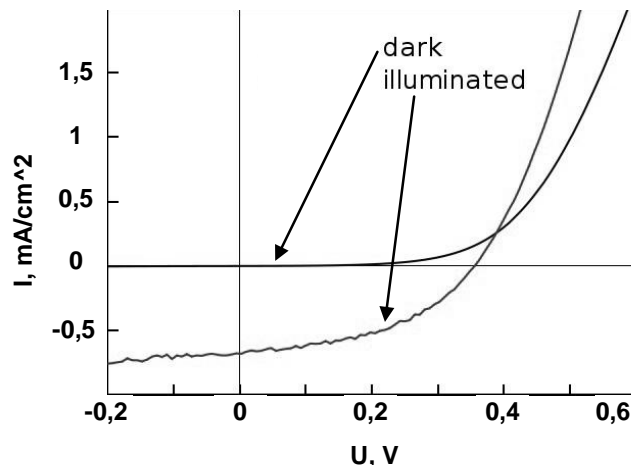


Fig. 5. *I-V* characteristics of inverted phthalocyanine - C_{60} bulk-heterojunction solar cells with and without light modification.

illustrated in Figure 6. Cathodic photocurrents were observed upon irradiation of the modified gold electrodes. However, strong excited state quenching of the porphyrin by the gold surface is the limiting factor that prevents attaining higher charge separation quantum yields.

This is usually suppressed drastically when modifying fullerenes is transformed by chemical doping into a highly conducting state. However, modifying fullerenes also luminesced and essentially maintained the features of modifying fullerenes. Here, the reduction of the long-wave emission band was in agreement with a more planar conformation

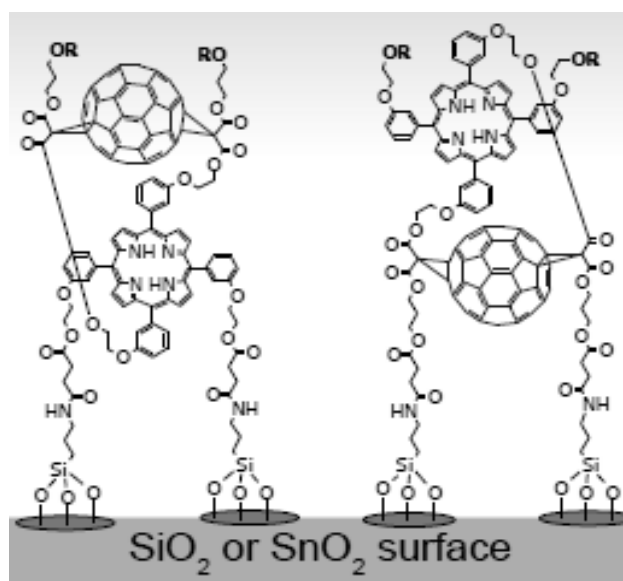


Fig. 6. Molecular layer can be assembled on surface of metal or semiconductor electrode by covalent linking the molecules to the surface. Methoxysilane groups can be used for selfassembling on SiO_2 surface [1].

of modifying fullerenes. It is highly remarkable that the presence of 50 % of fullerenes in the modifying fullerenes composite, which make it highly conductive, did not result in a quenching of luminescence.

Studied the optical activity properties modifying fullerenes solutions. It is well known that the addition of acids transforms fullerenes into the corresponding emeraldine salt, whose backbone then adopts a modifying structure which is responsible for its optical activity. Therefore, the starting point was the stable, modifying fullerenes solution. To this solution, I added the modifycal-camphorsulfonic acid. In contrast to the addition of *HCl*, which results in precipitation of the fullerenes, the addition of camphorsulfonic acid resulted in a stable, solution of the corresponding emeraldine salt modifying fullerenes. Figure 6a shows the *UV-Vis* spectrum of the resulting modifying fullerenes composite and that of emeraldine salt for comparison. The three characteristic bands at 345, 415, and 810 nm are associated with *p-p**, polaron-*p** and *p*-polaron band transitions of emeraldine salt. The broad *p*-polaron band at 810 nm is typical of an arrangement of polymer chains in the “compact coil” form [5, 7]. Modifying fullerenes essentially showed the same features, as well as a dominant band at 295 nm. As in the case of modifying fullerenes, this band corresponded to the *p-p** transition centred on the Quindio unit and was related to the coating of modifiable onto fullerenes.

Furthermore, both solutions had become optically active (shows, Figure 5). These observations are consistent with the polymer adopting a “compact coil” conformation. The circular dichromatic spectrum for modifying fullerenes showed that the polymerization of aniline in the presence of fullerenes and doping did not inhibit the polymer’s ability to become optically active. The effects of introducing optical properties into modifying fullerenes composites and its technological implications are being investigated.

Soluble modifying fullerenes composite has enhanced conductivity and improved thermal stability. It is also luminescent, optically active and can be processed from solutions into films, coatings and fibres. Depending on the synthesis conditions, the bithiazole based polymers exhibited optical band gaps ranging from 2,62 eV to 1,77 eV and the copolymers displayed multichromism within a wide span of the visible spectrum. The copolymers revealed short switching times and useful optical contrast of 0,6 S and 54 %, respectively. These devices exhibited low switching voltages and

switching times with reasonable stability under atmospheric conditions. I believe that these findings provide the basis for novel smart organic materials of great use in smart optoelectronic applications and devices.

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