Electron tranfers in fullerenes and nanotubes

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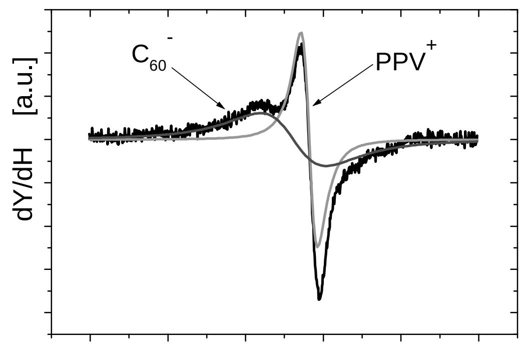
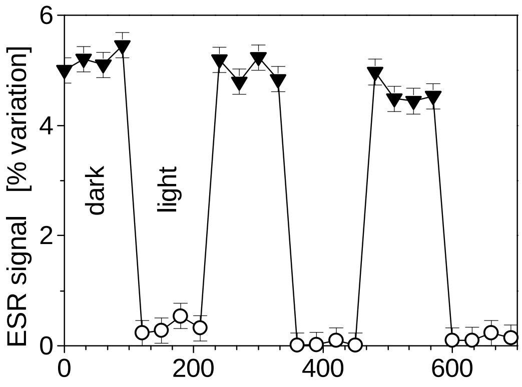
Because of their peculiar electronic properties, fullerene C_{60} and carbon nanotubes (CNT) are being intensively studied in view of their use in molecular electronic devices. Fullerene are able to reversibly accept up to five electrons, carbon nanotubes can behave as ballistic conductors or semiconductors, all properties desirable for many applications. We shall illustrate how C_{60} can be used in organic photovoltaic cells and how CNT can serve as magnetic couplers.

It has been proven that the incorporation of C_{60} in organic photovoltaic cells greatly improves both the efficiency of light conversion and the electronic conduction. Still, the making of good quality thin films is difficult with pure C_{60} and the use of C_{60} derivatives does not always grant significant improvement. Here, new amphiphilic fullerene derivatives ($AmphC_{60}$) and conjugated oligomers will be reported. In order to gain a better understanding of the intermolecular interactions, the photovoltaic cells made of these compounds are processed with the Langmuir-Blodgett technique which gives a very precise control of the molecular orientation. The designed amphiphilic fullerene cyclic bisadducts show very good spreading characteristics and reversible compression/expansion behaviour. The encapsulation of the fullerene core in its addends actually prevents the aggregation usually observed for other amphiphilic fullerene derivatives. Transfer of mono- and multi-layers of these bisadducts onto solid substrates has also been studied, and excellent quality LB films are readily processed. Photoinduced electron transfer has been observed in composite LB films of the $AmphC_{60}$ and conjugated oligomers, and these donor-acceptor composites have been used to prepare photovoltaic devices. The results will be discussed. We shall also consider the use in photovoltaic applications of LB films with alternating layers of amphiphilic PPV derivatives and $AmphC_{60}$, which appear as good candidates in terms of efficiency, owing to the excellent coupling between the layers.



ESR signal from an irradiated composite cell. The fine line comes from the radical anion C_{60}, the broad one from the PPV^+.

Molecular magnetism is a promising yet challenging field of research. Molecules offer the enticing promise of a magnetic material possessing optical or electrical supplementary properties. Amongst untackled problems is the question of coupling between radicals, which ultimately governs the bulk behaviour. Intramolecular coupling is usually the fact of delocalised π electrons whereas intermolecular coupling comes from short-range contacts between neighbouring molecules. As electrons in overlapping orbitals have a natural tendency to be antiparallel, anti-ferromagnetic interactions result most of the time of such contacts. High temperature ferromagnetism remains the holy grail for researchers in the field, the highest Curie temperature for a purely organic material being today 1.48K. This can certainly be ascribed to the lack of a good understanding on how intermolecular coupling works. Mixing of fullerene C_{60} with tetrakis(dimethylamino)ethylene has led to a crystalline complex exhibiting ferromagnetism below 16K. This result exemplifies the potential role of π electrons as transmitters of ferromagnetic exchange interaction in organic materials. Single-walled carbon nanotubes (SWNT) have original electronic properties because of their peculiar structure and it has been shown that nanotubes can coherently transport spin-polarized electrons over long distances(250nm). In this context we decided to investigate SWNT as magnetic couplers between radicals. The commercially available TEMPO radical (nitroxide family), chosen mainly because of its stability, has been easily grafted to SWNT's. The first measurements having revealed some photosensitivity of the ESR signal we then tried wrapping conjugated polymers around the SWNT's, following the work of Star *et al.*. These authors having shown that such a wrapping enabled the gating of the SWNT's conductivity, we saw a possibility of modifying the inter-radical coupling. Light switching of the intramolecular coupling of radicals has already been demonstrated but with photochromic couplers. It will be shown that associating PmPV to the SWNT-TEMPO system enhances the photosensitivity. Moreover, the photosensitivity is kept even when the radicals are not covalently attached to the nanotubes, which is surprising.



Variation of the integrated ESR signal of polymer-wrapped SWNT's with end-grafted radicals under light irradiation.