

Photoinduced charge and energy transfer involving fullerene derivatives

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In this feature article, a brief overview over the photoinduced energy and charge transfer mechanisms involving fullerenes will be presented. The photoinduced charge separation between organic donor and acceptor molecules is the basic photophysical mechanism for natural photosynthesis and nearly all organic solar cell concepts. We will give a short introduction to the mechanisms of excited state charge transfer and resonant energy transfer and present examples of relevant applications in organic optoelectronics and photodynamic tumor therapy.

I. Introduction

The discovery of the truncated icosahedral symmetry and high stability of Buckminsterfullerene C_{60} (Fig. 1a)^{1,2} in the first terrestrial experiments after its discovery in interstellar dust was awarded with the Nobel prize in 1996 for Curl, Kroto and Smalley. Since its availability in large quantities by the arc discharge process introduced by Krätschmer and coworkers,³ a lot of research has been dedicated to this class of molecules.

The advancement of fullerene chemistry introduced by Wudl and coworkers⁴ led to several routes to attach all kinds of chemical groups to the fullerene cage, yielding a vast number of

available fullerene derivatives. This opened up various applications in science and technology from bio-lifesciences to organic optoelectronic devices.⁵⁻⁷ The chemical structures of the fullerene derivatives mentioned in this text are depicted in Fig. 1.

The highly conjugated nature of fullerene molecules leads to interesting electronic properties. A close packed film of C_{60} and many of its derivatives shows direct bandgap semiconducting behaviour with a symmetry forbidden valence band–conduction band transition.⁸ This results in a low absorption coefficient just above the energy gap of 1.8 eV. Even though the fullerene semiconductors show a narrow band width in solid state, high electron mobilities can be exploited for example in organic thin-film field-effect transistors.⁹⁻¹¹

On a single molecule level, fullerenes show a high electron affinity resulting from an energetically deep lowest unoccupied molecular (LUMO) level of -4.3 eV *versus* vacuum.¹² In contact

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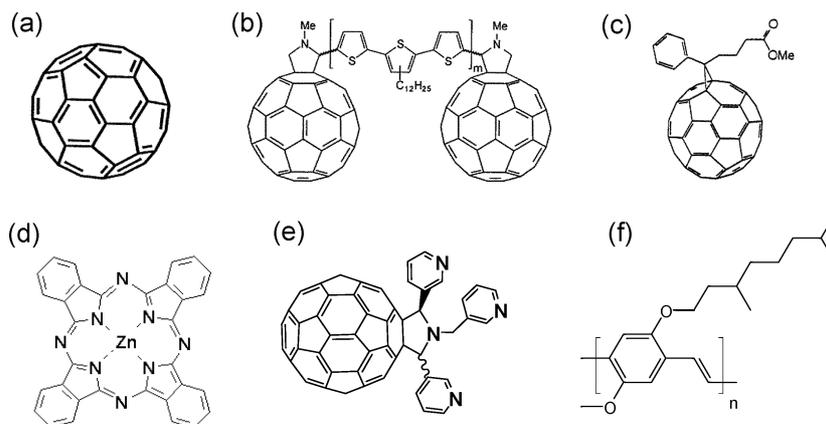


Fig. 1 (a) Buckminsterfullerene C_{60} ; (b) the fullerene–oligothiophene–fullerene triad used in ref. 39; (c) [6,6]-phenyl- C_{61} butyric acid methyl ester (PCBM); (d) zinc–phthalocyanine; (e) the pyrrolidino fullerene with pendant pyridyl groups used in ref. 65,67; (f) MDMO–PPV (poly((2-methoxy-5-(3,7-dimethyloctyloxy)-*p*-phenylene) vinylene).

with organic molecules having a higher lying LUMO level, this high electron affinity can lead to a favoured electron transfer process to the fullerene.

There are reports on ground state electron transfer occurring between fullerenes and electron donating molecules.¹³ This has to be distinguished from the photoinduced or excited-state charge transfer that happens only upon excitation of the charge transfer donor^{14,15} and is the basis for the use of fullerenes as electron acceptors in organic solar cells.^{16,17}

Fullerenes and their derivatives show a strong absorption around 3.7 eV typical of a π -conjugated organic molecular system. Although the large extension of the conjugation leads to a comparatively low optical energy gap of around 1.8 eV, the absorption of C_{60} remains low in the visible part of the spectrum due to the symmetry forbidden $h_u \rightarrow t_{1u}$ transition.^{13,18} In the higher fullerenes like C_{70} and C_{84} , this high degree of symmetry is broken and the low energy transitions become more prominent.¹⁹

The luminescence quantum yield of fullerenes in solution as well as in films is usually very low. This is due to the forbidden LUMO–HOMO transition and a very efficient intersystem crossing giving rise to an exceptionally high triplet yield. Due to this effect, fullerenes are of little use in light emitting devices. Finally, the confined nature of the π -electrons on the fullerene cage leads to very pronounced nonlinear optical properties of these molecules.^{20,21}

In the following, we will concentrate on photoinduced energy and charge transfer interactions involving fullerenes. Furthermore we will show examples from different applications where these mechanisms are utilized in promising technological approaches.

II. Resonant energy transfer

II.1. Background

More than 50 years ago, Theodor Förster described the interaction between two photoactive species like molecules or nanoparticles *via* a coupling of their transition dipoles in an elegant semiclassical theory.^{22,23} The implications of his theory became apparent with

the discovery that nature uses the energy transfer process to harvest photons for the photosynthesis process.²⁴ In biological science, Förster resonant energy transfer is widely used in optical techniques for detection of bioactivity and determination of protein folding mechanisms.²⁵

A donor molecule in the excited state energetically in resonance with a nearby acceptor molecule can efficiently transfer its energy. After the transfer, internal relaxation in the acceptor molecule takes place and the excitations are not in resonance any more. If donor and acceptor molecules are different species, the dipolar transitions are usually out of resonance by far more than k_T after the transfer, making a back transfer highly improbable. Thus, this energy transfer mechanism is unidirectional and can be used to move energy radiationless over distances of tens of nanometers with an appropriate cascaded energy gap structure.^{26,27} This is also exploited by natural photosynthesis to concentrate the energy on the photosynthetic reaction center, which has a limited absorption cross-section.²⁴

This energy transfer described by Förster's theory does not require a direct coupling of the wavefunctions as it is triggered by the interaction of the electrical fields generated by the transition dipoles of the participating chromophores. The rate of energy transfer is given by the Förster formula:

$$k_{\text{EnT}} = C \frac{\kappa_{D^*A}^2 \Phi_{D^*}}{n^4 R_{DA}^6 \tau_{D^*}} \int S_D(\nu) \frac{\epsilon_A(\nu)}{\nu^4} d\nu$$

where n is the index of refraction, C is a constant, κ_{D^*A} is an orientation factor ranging between -2 and 2 , Φ_{D^*} is the luminescence quantum efficiency of the donor, τ_{D^*} the donor luminescence lifetime, $S_D(\nu)$ the normalized donor emission spectrum, $\epsilon_A(\nu)$ the acceptor extinction coefficient, ν the frequency and R_{DA} the distance between donor and acceptor.

Important factors are the distance between donor and acceptor, the overlap and strength of the donor emission and acceptor absorption as well as the orientation of the dipoles and the dielectric surrounding. For a system of specific chromophores inside a matrix usually the leading dependency is in the distance,

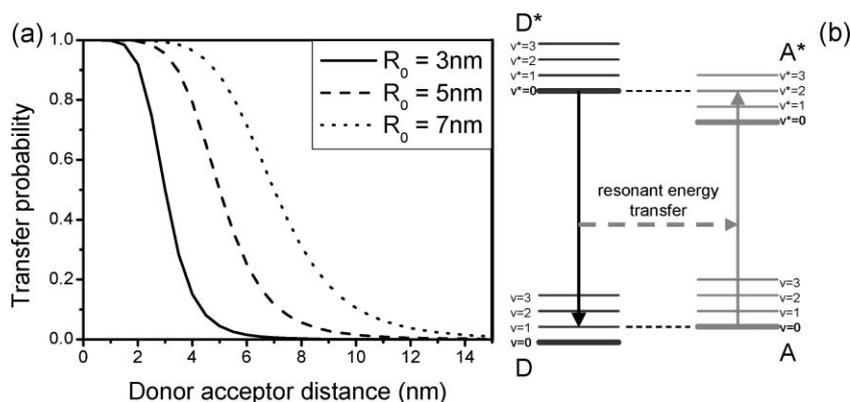


Fig. 2 (a) Distance dependence of the energy transfer probability according to Förster's theory; (b) energy level diagram illustrating the resonance condition for energy transfer.

so the formula can be abbreviated:

$$P = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6}$$

where R_0 is the so called Förster radius giving the distance between donor and acceptor with an energy transfer probability of 50%. The dependency of the energy transfer probability P on the distance between donor and acceptor is shown in Fig. 2a, an energy level diagram illustrating the resonance condition in Fig. 2b.

Upon illumination, the excitation energy is transferred from the donor to the acceptor molecule. This leads to a quenching of the donor emission and—in contrast to the charge transfer described below—an increase in the acceptor luminescence. If the absolute values of luminescence intensity are hard to quantify, another approach is to look at the temporal decay of the luminescence. The energy transfer shortens the lifetime of the donor emission. In the case that the donor has a comparable or longer luminescence lifetime than the acceptor, the acceptor lifetime will be increased. If it is shorter, the acceptor lifetime will be unaffected.

Usually, the change in donor luminescence intensity or lifetime is the best parameter to quantify the transfer probability. An increase of the acceptor luminescence intensity as well as an unaffected or increased acceptor luminescence lifetime are very strong indications for energy transfer as opposed to charge transfer, which would be detrimental for the donor as well as acceptor luminescence.

Another method to discriminate between energy and charge transfer is to increase the distance between the two interacting species. The much longer range of the Förster type of energy transfer will often be clearly distinguishable. Charge transfer generally depends exponentially on the distance, while resonant energy transfer shows a dependence on the distance to the sixth power.

As there are no charges created in the resonant energy transfer process, charge sensitive techniques such as light induced electron spin resonance (L-ESR) or photoinduced absorption (PIA) can be used to distinguish this phenomenon from charge transfer and radical generation mechanisms.

II.2. Energy transfer involving fullerenes

II.2.1. Fullerenes as energy transfer donors. Compared with many photoactive organic substances, fullerenes have a relatively

low energy gap of about 1.8 eV. Additionally, they show only a weak luminescence due to the symmetry forbidden $S_1 \rightarrow S_0$ transition and a fast intersystem crossing to the triplet state. Therefore, systems in which fullerenes can act as energy transfer donors with significant efficiency are very rare with one notable exception.

The triplet state of C_{60} can undergo a very efficient triplet energy transfer to a ground state triplet oxygen molecule 3O_2 , transferring it into a very reactive singlet oxygen molecule 1O_2 .^{18,28} The whole mechanism is depicted in Fig. 3.

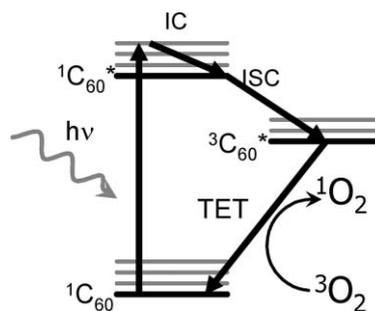


Fig. 3 Energy level diagram illustrating the generation of singlet oxygen (1O_2). Light transfers C_{60} from the ground state ($^1C_{60}$) to the first excited state ($^1C_{60}^*$). Internal conversion (IC) and intersystem crossing (ISC) lead to the formation of a triplet state ($^3C_{60}^*$), which can decay efficiently in the presence of oxygen molecules (3O_2) via triplet energy transfer (TET) to produce singlet oxygen (1O_2).

Singlet oxygen can have detrimental as well as beneficial effects. In many applications of organic semiconducting materials, the reaction of singlet oxygen with hydrocarbon chains is deteriorating the device properties.^{29–31} This is especially important for organic solar cells where a donor material, usually a polymer chain, is doped with fullerenes as acceptor molecules (see III.2.2). The photogeneration of singlet oxygen that reacts with the donor could be one of the reasons for the low stability of some of these devices in the presence of oxygen.³²

In biomedical applications, the high yield of singlet oxygen formation makes fullerenes interesting for photodynamic tumor therapy or other applications where phototoxicity is required.^{28,33,34} A severe disadvantage is the low absorption of most fullerenes in the transparency window of living tissue from 600 to 800 nm as well as the low solubility in water. The second problem is being addressed by the synthesis of water soluble fullerenes,³⁵ but

unfortunately, these often show a severely reduced singlet oxygen quantum yield as the substituents disturb the π -conjugation of the fullerene cage.³⁶

The low absorption in the red part of the spectrum can be overcome either by attaching the fullerene to an absorbing species such as a porphyrin³⁷ or by using two-photon excitation which additionally allows for a depth control of the photoactivated volume.³⁸

II.2.2. Fullerenes as energy transfer acceptors. A prerequisite for an energy transfer acceptor is an equal or lower energy gap than that of the donor. Fullerene derivatives have an absorption range reaching to over 700 nm, as can be seen in Fig. 4 for the example of the fullerene derivative [6,6]-phenyl- C_{60} butyric acid methyl ester (PCBM, Fig. 1c). But the symmetry restrictions with the resulting low oscillator strength of absorption for energies below 2.5 eV severely limits the characteristic radius R_0 of the energy transfer from even a highly luminescent donor. In combination with many organic materials, the competing photoinduced charge transfer process¹⁴ can be much faster at short distances so that the energy transfer plays no role.

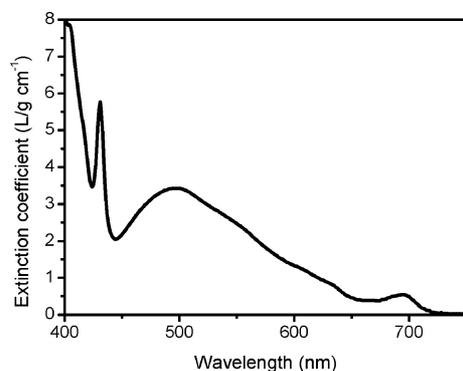


Fig. 4 Extinction coefficient of the fullerene derivative PCBM in toluene solution.

Some combinations of fullerenes and organic molecules nevertheless clearly yield energy transfer instead of charge transfer upon excitation. Janssen and coworkers³⁹ have found that in a fullerene–oligothiophene–fullerene triad (Fig. 1b) in toluene, energy transfer from the oligothiophene to the fullerenes is the predominant photoinduced transfer reaction. Calculations of the free energy change for charge separation using the Weller formalism confirm that charge transfer in this system is unfavourable and therefore, energy transfer dominates. Noteworthy is the fact that a more

polar solvent like benzonitrile can change this picture and lead to a dominant charge transfer process.⁴⁰

Another report of energy transfer from an organic molecule to a fullerene is given by Martini *et al.*, who studied a dyad of C_{60} linked to a perylene derivative *via* a pyrrolidine linker.⁴¹ The authors report a near equal proportion of charge and energy transfer in this system, as can be seen from luminescence and ultrafast pump–probe measurements. In a later study on a similar system Hua *et al.* see a predominance of energy transfer in photoluminescence studies and additionally claim that they see evidence for the presence of a weak charge transfer in photoconductivity studies.⁴² These papers underline the competing nature of the two processes that are often simultaneously possible in a system of two organic chromophores in close contact.

A very recent study of Liu and coworkers elaborates the role of energy transfer processes that might play a role in organic donor–acceptor bulk heterojunction solar cells.⁴³ They studied a model system consisting of a dye (Nile red) and the fullerene derivative PCBM commonly used in organic solar cells. The dye is considered to have similar luminescence properties and energy levels as conjugated polymers used in organic solar cells.

The energy levels and the sample setup for this experiment are depicted in Fig. 5a. Both materials are mixed into an insulating polystyrene matrix with different concentrations of PCBM. The quenching of the dye photoluminescence is recorded for increasing concentrations of PCBM and compared with model calculations according to Förster's theory for energy transfer and to Perrin's equation with a quenching efficiency of unity below a certain radius.⁴⁴ According to these calculations, energy transfer with a characteristic radius $R_0 \approx 3$ nm is the dominant transfer process (Fig. 5b). This means that in a solar cell, excitations on the polymer do not have to diffuse all the way to the polymer–fullerene interface, as there is an efficient long range energy capture mechanism. Furthermore, this mechanism could lead to detrapping of excitons caught in a localised low energy state on the polymer. Both mechanisms are beneficial for the performance of an organic solar cell.

In optimized organic bulk heterojunction solar cells, the efficiency of charge separation between polymer and fullerene is close to unity. An energy transfer process from polymer to fullerene would appear in effect as if there is an increased exciton diffusion length. The low exciton diffusion length below 10 nm is often a limiting parameter for photocurrent generation in organic solar cells. The authors conclude that the increased contribution of long-range energy transfer will have to be considered in new organic solar cell concepts.

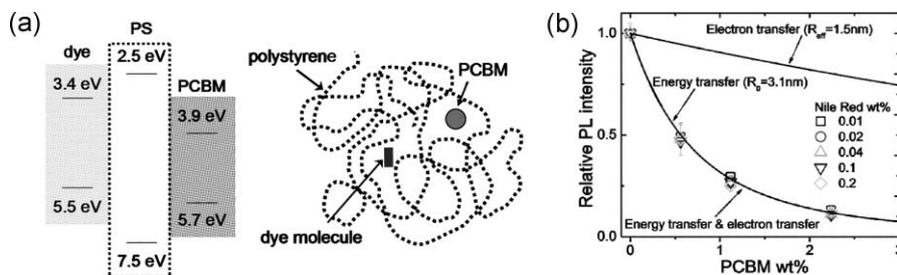


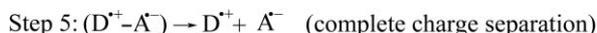
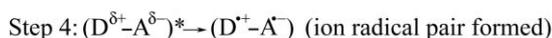
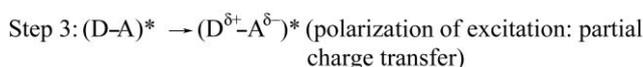
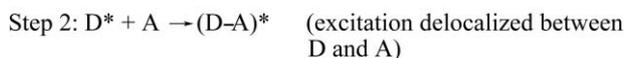
Fig. 5 (a) Energy level diagram of the two chromophores and the insulating matrix and sample configuration; (b) evolution of the dye fluorescence with the concentration of PCBM added in the film compared with model calculations for charge and energy transfer indicating a dominance of resonant energy transfer (Reproduced from ref. 43, Copyright 2006 American Institute of Physics AIP).

III. Photoinduced charge transfer

III.1. Background

Photoinduced charge transfer reactions have been extensively investigated in many fields of science for a long time as it is of fundamental interest for understanding the photophysics and photochemistry of excited states in organic molecules. Furthermore, it is an important step in photosynthetic energy conversion in green plants.^{45,24}

A basic description of the photoinduced charge transfer between a donor molecule D and an acceptor molecule A can be described as follows:



The example given here is for electron transfer from excited donor onto the acceptor. Alternatively, a hole transfer from an excited acceptor onto a donor can be written equivalently. A and D have to be either covalently bound (intramolecular charge transfer) or spatially very close (intermolecular charge transfer). To initiate step 2 in the above scheme, the electronic wavefunctions of A and D have to have a significant coupling, so the distance between the molecules must be small.^{46,47} Also the orientation between the participating molecules is sometimes of great importance.⁴⁸

The relevant factor for the occurrence of step 4 is the alignment of the energy levels of the participating molecules. Only if the offset between the LUMOs (for electron transfer) or the HOMOs (for hole transfer) of donor and acceptor is large enough to overcome the coulombic attraction between the charges, charge separation will be possible. A scheme of the configuration for electron and hole transfer is depicted in Fig. 6. In general, the energetics and kinetics of the photoinduced charge transfer can be described by the theories of Marcus and Jortner taking into account the orientation and the distance between the donor and acceptor chromophore.⁴⁹⁻⁵²

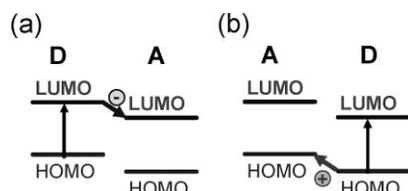


Fig. 6 (a) Energy level alignment necessary for electron transfer from D to A; (b) energy level alignment necessary for hole transfer from D to A.

If all requirements are met, charge transfer can be very efficient with transfer rates as high as $k_T = 10^{12} \text{ s}^{-1}$.^{13,46,53} The charge transfer state can be metastable due to a fast delocalization of the charge carriers on one or both of the molecules.⁵⁴

As an efficient charge transfer happens on a faster timescale than the radiative decay in usual organic chromophores such as conjugated polymers, a first indication of photoinduced charge transfer is the quenching of the luminescence and decrease of luminescence lifetime for both compounds when they are brought in close contact with each other.

Another method to detect and quantify photoinduced charge transfer is photoinduced absorption measurements. Upon excitation, the absorption spectrum of both single compounds shows ground state bleaching and additional excited state absorptions. In a donor-acceptor mix with efficient photoinduced charge transfer, additional features corresponding to the charged species will appear. These can be compared to known absorption features of the ionized single molecules for identification. In a time-resolved measurement, the lifetime of these features will correspond to the lifetime of the charge separated state. From the decay of the excited state absorption, the charge transfer rate can be derived.^{53,54}

Finally, light induced electron spin resonance (L-ESR) studies can give very definite evidence of photoinduced charge transfer. Under illumination, a mixture of donor and acceptor molecules suitable for an efficient charge transfer will show ESR signals for the radical cations or anions. The temperature dependence will give information on the activation energy for the charge transfer process and the back transfer reaction.⁵⁵

If at least one of the materials undergoing photoinduced charge transfer is an organic semiconductor, the charge transport properties of a solid phase blend will be significantly altered upon illumination due to the charges generated on the molecules. This effect usually leads to an enhanced photoconductivity and can be described as "photodoping". If both materials (donor as well as acceptor) are semiconducting, it is possible to build photodiodes and solar cells, where charges are generated under illumination at the interface between a donor and an acceptor material and transported to the electrodes.⁵⁶

III.2. Photoinduced charge transfer involving fullerenes

III.2.1. Fundamental aspects. Fullerenes with their triply degenerate, low lying LUMO at -4.3 eV versus the vacuum energy level are excellent electron acceptors capable of accepting as many as six electrons.¹² This leads to the formation of ground state charge transfer states with a variety of strong electron donating substances. Even a larger number of substances undergo photoinduced electron transfer to fullerenes, such as conjugated polymers,¹⁴ metal phthalocyanine⁵⁷ or porphyrin molecules.⁵⁸ A great advantage of using fullerenes as photoinduced charge transfer acceptors for other molecules is their high symmetry that leads to a good contact with the neighbouring molecules almost independent on the fullerene orientation.

Often this photoinduced electron transfer from a donor onto the fullerenes is also accompanied by an efficient photoinduced hole transfer from the fullerene. The HOMO level of C_{60} at about -6.1 eV versus the vacuum energy level¹² is also significantly lower as in most of the organic molecules mentioned above, so the requirement for a photoinduced hole transfer from the fullerene can be fulfilled. And indeed, Wang and coworkers found signatures of an efficient photoinduced charge transfer in a mix of polyvinylcarbazole (PVK) and C_{60} under visible illumination, where only C_{60} is photoactive.⁵⁹

One of the most striking aspects of the photoinduced charge transfer between organic donor molecules, especially conjugated polymers and fullerenes is the long lifetime of the charge separated state. Under favourable conditions, the photoinduced charge transfer is ultrafast with rates above 10^{12} s^{-1} while the back transfer is almost ten orders of magnitude slower at room temperature.

One way to understand this feature is to assume an instant delocalization of the generated charges in the donor and acceptor π -electron systems reducing the probability for geminate recombination.^{14,54} In a very recent study by de la Escosura *et al.*,⁶⁰ a covalently linked dyad between a Zn–phthalocyanine and a C_{60} molecule was investigated (Fig. 7, molecule 1). As the two moieties are very close together, ultrafast photoinduced charge transfer happens, that can be monitored by photoinduced absorption measurements and luminescence quenching. The lifetime of the charge separated state was determined by time resolved photoinduced absorption measurements to be 130 ns.

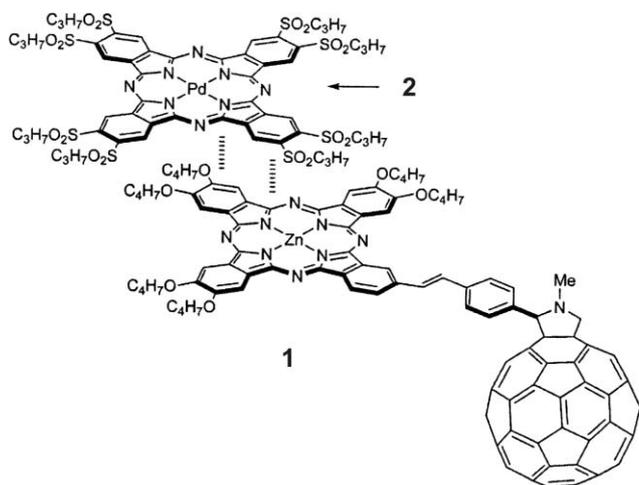


Fig. 7 Zn–phthalocyanine–fullerene dyad (1), Pd–phthalocyanine (2) and the proposed donor–acceptor complexation (dashed lines) leading to a stabilization of the charge separated state inside the dyad (Reproduced from Ref. 60, Copyright 2006 American Chemical Society ACS).

A Pd–phthalocyanine compound (Fig. 7, molecule 2) with strong electron accepting properties has been shown in a previous work to self-assemble in a supramolecular complex with the Zn–phthalocyanine used in the dyad.⁶¹ Upon mixing the dyad and the Pd–phthalocyanine in solution, the complexation takes place resulting in the triad indicated by the dashed lines in Fig. 7. This triad shows a significantly longer lifetime of the charge separated state of 475 ns. The authors claim that the complexation leads to a strong electronic coupling between the two phthalocyanine moieties, thus allowing the radical cationic charge generated by the photoinduced charge transfer to delocalise further away from the counter charge on the fullerene. This leads to a stabilization of the charge separated state.

III.2.2. Applications. The most important application of photoinduced charge transfer to and from fullerenes is the possibility of building donor–acceptor heterojunction photodiodes from fullerenes with organic semiconductors^{56,57} or even inorganic semiconductor nanoparticles.⁶² In these concepts, the fullerenes

act as electron acceptors or hole donors as well as electron transport material.

A predominance of the photoinduced charge transfer over all other decay processes is the first necessity for materials considered for usage in donor–acceptor bulk heterojunction solar cells. This is possible by engineering of the energetic properties of the electron donor and hole acceptor material by chemical synthesis. On the other hand, the materials have to be intimately mixed, as the charge generation will only take place at the direct interface between donor and acceptor molecules.

In organic donor–acceptor bulk heterojunction solar cells using the conjugated polymer MDMO–PPV (poly((2-methoxy-5-(3,7-dimethyloxy)-*p*-phenylene) vinylene) and the highly soluble fullerene derivative PCBM, a strong increase in photocurrent and overall performance was observed upon changing the common solvent from which the compounds are cast from toluene to chlorobenzene.⁶³ Further investigations showed that a nanoscale phase separation takes place during the film formation yielding a nanomorphology that is very sensitive on the casting conditions. Studies performed with AFM, Kelvin probe microscopy and SEM (Fig. 8) show that the two compounds strongly phase separate in the case of a blend cast from toluene, while using chlorobenzene yields a much finer mixture.^{64–66}

The connection between the nanomorphology and the performance of an organic solar cell can be understood partly by considering the interface for charge transfer. In the very coarse blends cast from toluene, the interfacial area at which excitations can be separated into electrons and holes is much smaller. A direct indication of this can be found in the luminescence of the films, as shown in Fig. 9.

The luminescence of the PCBM in the blend cast from toluene is much stronger than in the blend cast from chlorobenzene. This indicates that due to the coarse phase separation in the toluene blend, not all of the PCBM is in close enough contact with the polymer to undergo a charge transfer. As in these solar cells a significant amount of light absorption is in the PCBM phase, the amount of generated charge carriers and therefore the photocurrent is reduced in the coarsely phase separated blend.

However, a finer phase separation and smaller grain size does not guarantee increased photocurrent, since the photogenerated charge carriers will have to overcome much more interfaces during their travel in a fine mixture. Thus, there will be a complicated counterbalance between charge separation efficiency and charge transport in a given nanomorphology.

In a recent study, the interface in a bilayer zinc–phthalocyanine:fullerene solar cell was modified by using a pyrrolidinofullerene compound with chelating pyridyl groups (PyF) that can interact with the Zn atom in the Zn–phthalocyanine (ZnPc) molecule.⁶⁷ The two molecules are shown in Fig. 1d and 1e. In previous studies, the pyridyl nitrogen of PyF was shown to coordinate to the zinc atom in a Zn–porphyrin compound.⁶⁸ A single crystal X-ray structure of the complex between Zn–porphyrin and a similar pyrrolidinofullerene compound is shown in Fig. 10.

To verify that a similar complexation takes place also with ZnPc, photoluminescence quenching studies were performed.⁶⁹ The PyF is compared with PCBM, a different soluble fullerene derivative (Fig. 1c) without possibility for complexation. A Stern–Volmer

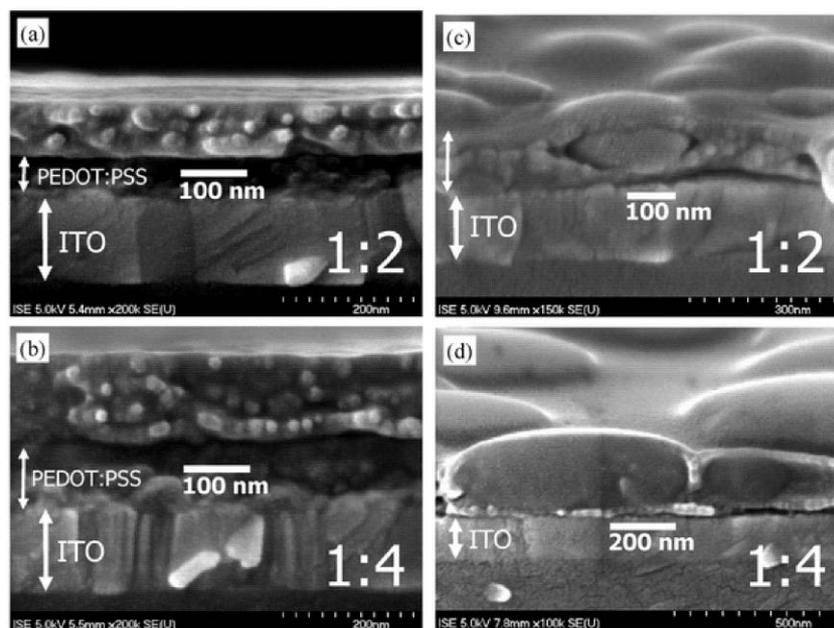


Fig. 8 SEM cross-section images of films of MDMO-PPV:PCBM blends cast from chlorobenzene (a, b) and toluene (c, d). Whereas chlorobenzene based blends are rather homogeneous, toluene cast blends reveal large PCBM clusters embedded in a polymer-rich matrix or skin-layer. Small features—referred to as “nanospheres”—are visible in all cases and can be attributed to the polymer in a coiled conformation. The blending ratio is depicted in the lower right corner (Reproduced from ref. 64, Copyright 2004 Wiley VCH).

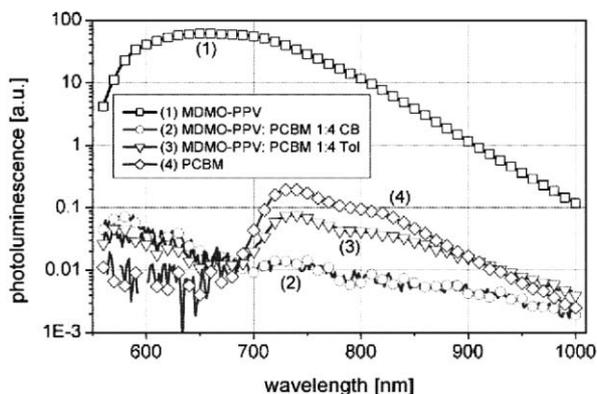


Fig. 9 Photoluminescence spectra of thin films on glass: MDMO-PPV (1), PCBM (4) and blends of MDMO-PPV:PCBM (1 : 4 by weight) cast from chlorobenzene (2) and toluene (3). The much stronger luminescence of PCBM in the films cast from toluene indicates large domains where PCBM does not undergo charge transfer due to the larger phase separation (Reproduced from ref. 64, Copyright 2004 Wiley VCH).

plot of the quenching ratio of the ZnPc luminescence in toluene solution in dependence on the concentration of added fullerene derivative is shown in Fig. 11. Upon adding PCBM, the quenching follows the behaviour expected for a purely diffusive encounter between the molecules in solution. A photoinduced charge transfer rate between 10^9 s^{-1} and 10^{10} s^{-1} can be estimated.

Upon adding PyF, the Stern–Volmer plot shows a superlinear dependence of the quenching on the fullerene concentration with a base quenching rate similar to PCBM. This corresponds to an attractive interaction between the molecules indicating the complexation. This is further substantiated by the observation of

significantly increased solubility of ZnPc in CH_2Cl_2 in the presence of PyF.⁶⁷

Solar cells fabricated by spincoating a thin layer of fullerenes on a 40 nm thick evaporated ZnPc film give strongly enhanced photocurrents for the usage of PyF in comparison to PCBM. Fig. 12a shows the I – V characteristics of typical solar cells made of a 40 nm thick layer of ZnPc with either PCBM or PyF spincoated on top under 100 mW cm^{-2} simulated AM1.5 illumination. While the open circuit voltage is about the same, the short-circuit photocurrent of the cell with PyF is nearly doubled in comparison with the one with PCBM.

This is confirmed by the corresponding incident photon to collected electron efficiency spectra shown in Fig. 12b. Even though the absorption spectra of the active ZnPc–fullerene layers are very similar, the conversion efficiency in the red part of the spectrum and therefore the white-light photocurrent of the device is greatly enhanced by the use of PyF. As the red light is mainly absorbed by the ZnPc, this indicates an enhancement of the electron transfer from ZnPc to PyF with subsequent charge separation in comparison with PCBM. As the main difference between the two fullerene derivatives is the ability of PyF to form coordination complexes with the zinc atom in the phthalocyanine, the conclusion is that this coordination can facilitate the charge generation at the interface between ZnPc and fullerene.

Further applications of photoinduced charge transfer between organic molecules and fullerenes are in an enhanced responsivity of photoactive organic field effect transistors (photOFET) when using a blend of a conjugated polymer with PCBM as semiconducting material.^{70,71} Additionally, Schlebusch *et al.* considered adding C_{60} to organic photoreceptor layers in xerographic applications such as photocopiers and laser printers to enhance the sensitivity.⁷²

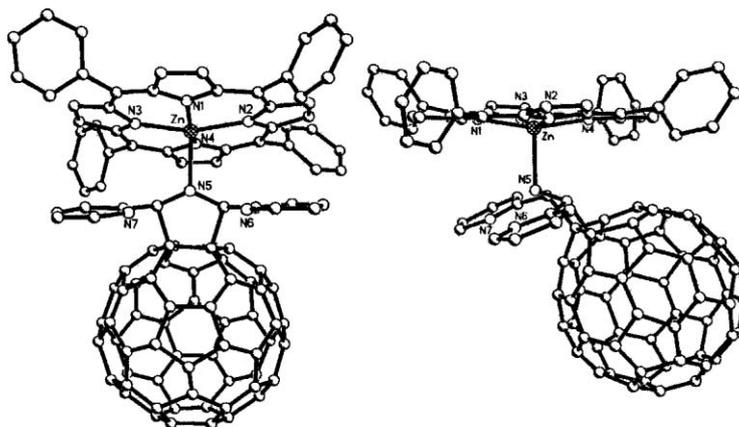


Fig. 10 X-Ray single crystal structures of the supramolecular complex between a PyF and a zinc-porphyrin molecule (Reproduced from ref. 68, Copyright 2004 Taylor and Francis Journals).

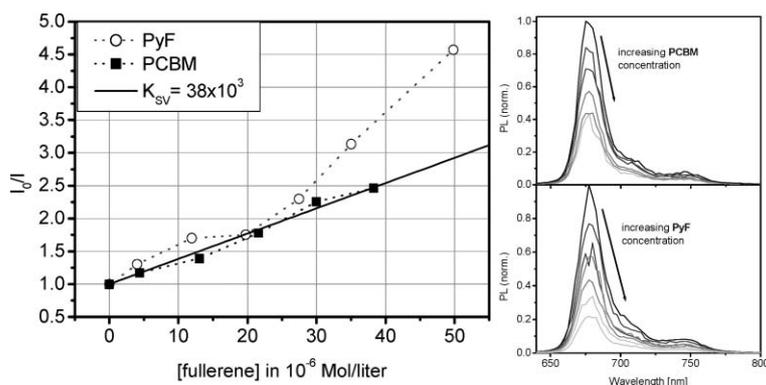


Fig. 11 Right: PL spectra of ZnPc in toluene with increasing amount of fullerenes added; left: Stern–Volmer plot for the quenching of ZnPc in toluene by PCBM and PyF (Reproduced from ref. 69, Copyright 2006 Taylor and Francis Journals).

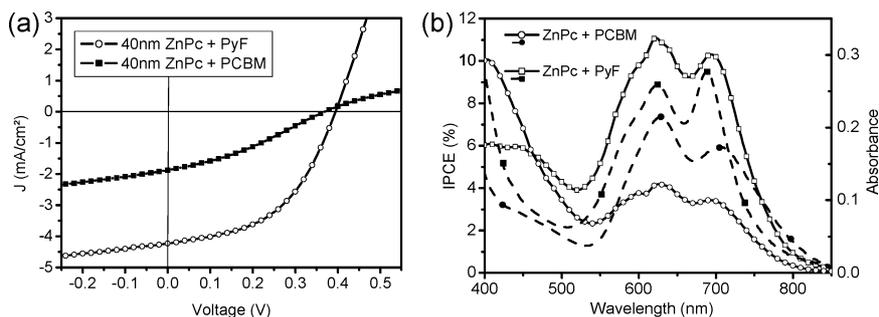


Fig. 12 (a) I – V curves of typical solar cells with an active layer of about 40 nm ZnPc covered with different fullerenes measured under 100 mW cm^{-2} of simulated AM1.5 irradiance; (b) incident photon to collected electron efficiency (IPCE) spectra of solar cells with an active layer of 25 nm ZnPc covered with PCBM (solid line, open circles) and PyF (solid line, open squares). Absorption spectra of 25 nm ZnPc covered with PCBM (dashed line, full circles) and PyF (dashed line, full squares) (Reproduced from ref. 67, Copyright 2005 American Institute of Physics AIP).

IV. Conclusion

Photoinduced energy as well as electron transfer processes play an important role in the photochemistry of organic and biological systems. In the fast growing field of organic optoelectronics, electron transfer processes are important in applications of photodiodes and photovoltaic cells as well as in phototransistors. Photoinduced energy transfer processes are important for light emitting diodes (LEDs) and light emitting organic field effect transistors as well as in photodiodes *via* “increasing” the exciton

diffusion length. Biodetectors widely use fluorescence emission as detecting mechanism and therefore such energy transfer processes are of fundamental interest in designing new and more efficient bio-sensors.

Due to their energetic properties, fullerenes are very versatile molecules with many possible uses in such photoinduced energy and electron transfer systems. The application of fullerenes in organic photovoltaics, where they are indispensable as photoinduced electron acceptors and electron transport materials as well as in photodynamic cancer therapy by their singlet oxygen generation

efficiency due to efficient energy transfer from their triplet state to triplet oxygen molecules, can be listed as important in future applications.

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