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Energy Transfer from CdSe/ZnS Nanocrystals to Zinc-Phthalocyanine for Advanced Photon Harvesting in Organic Photovoltaics

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Abstract Due to the limited spectral width of absorption in organic dyes, it is necessary to look for strategies to enhance the spectral photon harvesting in organic solar cells. Investigations of the energy transfer between zinc-phthalocyanine (ZnPc) and CdSe/ZnS core shell nanocrystals are performed and show a highly efficient energy transfer and no sign of a competing charge transfer mechanism. The dependence of the energy transfer efficiency on the length of the alkyl spacers around the nanoparticles is investigated.

The integration of semiconductor nanoparticles into a photodiode based on ZnPc yields increased sensitivity of the device in the green spectral range.

Keywords Energy transfer · Organic solar cells · Phthalocyanine · Semiconductor nanocrystals

The large scale availability of organic semiconductors now enables technological photonic applications such as organic light emitting diodes (OLEDs) and organic solar cells [1–3]. One of the most attractive properties of organic semiconductors is the possibility to combine and chemically alter the materials to fit a specific application.

Another material class allowing precise tailoring of optical and electrical properties are colloidal semiconductor nanomaterials. They exhibit strong optical absorption and high photoluminescence yield as well as solution processability. These properties can be tuned by changing the material, the size and the shape of the nanocrystals [4, 5]. The chemical properties of these nanoparticles are mostly determined by a shell of organic ligands that provide good compatibility with organic solvents and organic semiconductor matrices.

In bulk heterojunction organic solar cells, a solid state blend of a donor and an acceptor material is used, between which an ultrafast photoinduced charge transfer mechanism takes place. This photoinduced charge transfer facilitates the separation of excitations into free charge

carriers [6]. Both materials are usually active in charge transfer and charge transport and at least one of the materials has to be highly absorptive in the spectral range of the solar irradiation (chromophore). Especially a high absorption in a broad spectral region requires thick layers, but then the charge transport is likely to limit the solar cell performance. Since the mobilities are on the order of $\mu \approx 10^{-2} - 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the thickness is usually limited to around 100 nm.

Advanced photon harvesting concepts in which light absorption is separated from the materials providing charge generation and transport can overcome this problem. Resonant energy transfer from antenna molecules onto the photoactive components can play a major role in those concepts. Especially the long range energy transfer mechanism as described by the Förster theory [7] is applicable to funnel photon energy from light absorbing antenna materials onto the electrically active species. Exactly this strategy is implemented in natural photosynthesis systems using antenna molecules to absorb and funnel the energy into the photosynthetic reaction cen-

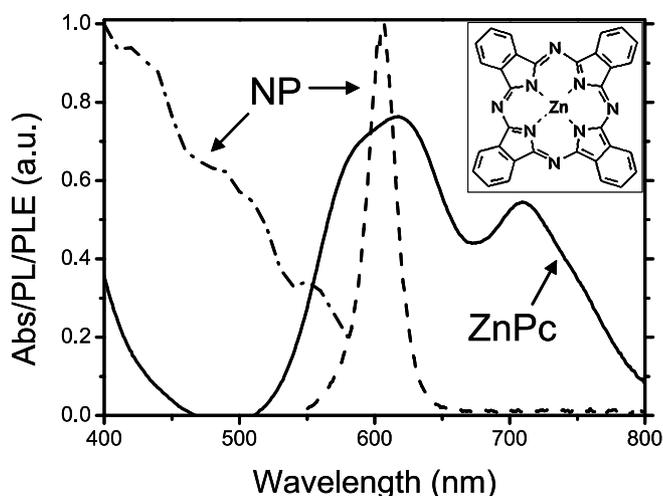


Fig. 1 Absorption spectra of a thin film of ZnPc (solid line), together with the photoluminescence (dashed) and photoluminescence excitation (dash-dotted) spectra of the CdSe/ZnS nanocrystals showing the possibility of energy transfer from the nanocrystals to the ZnPc due to the overlap between nanoparticle emission with the ZnPc absorption. Inset: the chemical structure of ZnPc

ter. Several reports exist in the literature using different approaches to combine energy transfer systems with photoinduced charge transfer [8–10] or to directly use natural photosynthetic complexes [11] in a solar cell.

Zinc-phthalocyanine (ZnPc) as photoinduced electron donor molecules can provide power conversion efficiencies above 3% in combination with C₆₀ fullerene as an electron acceptor [12–14]. ZnPc forms polycrystalline films upon vacuum evaporation which are semiconducting with strong absorption bands around 400 nm and between 600 and 800 nm. This material has an absorption lack around 500 nm (Fig. 1). Therefore, antenna systems absorbing wavelengths around 500 nm are fitting to this absorption profile of ZnPc.

As a photon harvesting antenna system, we use CdSe/ZnS nanocrystals with a high absorption cross section in the desired wavelength range as well as a strong luminescence above 600 nm, required for the energy transfer to the ZnPc. A second advantage is the organic ligand shell around the nanocrystals, electrically insulating them from the surrounding matrix. This ensures that the leading mechanism between the nanoparticles and the surrounding ZnPc matrix is energy transfer and not the charge transfer [16]. Charge transfer is not desirable, as the transport of the charges remaining on the nanocrystals is usually unfavourable.

In this work, we use steady state absorption and fluorescence spectroscopy to study the interaction between the two species. The nanoparticle ligands are altered to probe the dependence of the transfer efficiency on the distance between donor particle and acceptor matrix. Photodiodes with and without an intermediate nanoparticle layer are

compared and a significant spectral sensitization around 500 nm is observed.

The CdSe/ZnS nanocrystals were purchased as solution in toluene from NN-labs Inc. (www.nn-labs.com). Nominal diameter of the particles is 3.0 nm and the emission maximum in solution is at 605 nm. The CdSe core is epitaxially coated alternately with zinc (4 layers) and sulphur (3 layers) to passify surface states. The PL quantum yield in solution is approximately 40%. The original octadecylamine (ODA) ligands providing solubility were exchanged with a standard ligand exchange procedure [14] to *n*-alkanethiols of different length: *n* = 18 (T18), 16 (T16), 12 (T12), 9 (T9), 6 (T6).

Absorption spectra were taken with a Varian Cary 3G UV-Vis Spectrophotometer. The luminescence of the films was measured with a M.U.T “Tristan light” fiber spectrometer using a Coherent “Innova 400” Ar⁺-laser as 514 nm excitation source.

The energy transfer samples were produced by thermally evaporating 20 nm of ZnPc in high vacuum ($p < 10^{-5}$ mbar) onto a clean glass slide, followed by dropcasting of approximately 30 μ l solution of T12-coated nanocrystals and subsequent evaporation of another 20 nm thick film of ZnPc. A 40 nm thick film of ZnPc was evaporated under the same conditions onto a clean glass slide as reference.

The scattered nanoparticle samples were prepared by putting one drop of a solution of 2 mg nanoparticles (T18, T16, T12, T9 or T6) in 1 ml of toluene onto a clean glass slide (1.5 \times 1.5 cm²) rotating at 6000 rpm. Subsequently, on one half of the glass slide, a layer of 20 nm ZnPc is thermally evaporated in high vacuum. The quenching ratio was determined by averaging the nanoparticle photoluminescence of 5 points each on the parts of the glass slides with and without covering of ZnPc. The luminescence of the nanoparticles did not change significantly during several repetitions of the experiment independent of the coverage with ZnPc. Spin-coating the nanoparticles on top of a ZnPc film yielded similar quenching ratios, indicating that the deposition of ZnPc onto the nanoparticles does not alter the intrinsic PL efficiency.

The photodiodes were prepared by spincoating a layer of PEDOT:PSS (Baytron PH) onto an ITO-covered glass slide. These substrates were coated with a layer of 40 nm ZnPc by thermal evaporation in high vacuum. On some samples, approximately 25 μ l of T12 coated nanoparticle solution was dropcast. Then another 20 nm of ZnPc and 75 nm Al were evaporated to finish the diode structure. Charge separation in this photodiodes is not very efficient, but yields enough photocurrent to record the spectrally resolved photocurrent.

The Incident Photon to Collected Electron conversion efficiency spectra (IPCE) were measured by illuminating the active area of the samples with monochromatised and chopped light from a tungsten halogen lamp. The resulting

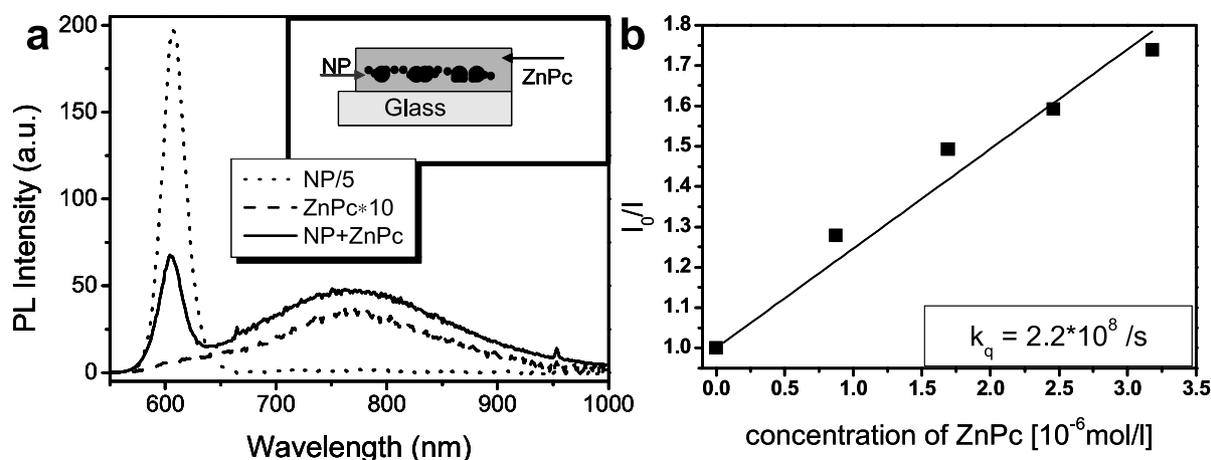


Fig. 2 **a** Photoluminescence spectra of a dropcast film of nanocrystals (dotted line 5 \times), a 40 nm thick evaporated film of ZnPc (dashed line 10 \times) and a 40 nm thick evaporated film of ZnPc with nanocrystals dropcast after 20 nm. Strong quenching of the nanocrystal luminescence and a significant increase of the ZnPc luminescence indicates efficient energy transfer. **b** Stern–Volmer plot of the quenching of the nanoparticle luminescence by addition of ZnPc molecules into the nanoparticle solution

modulated photocurrent is recorded by a lock-in amplifier. The lamp power is recorded with a silicon diode powermeter (Thorlabs PM100) and is between 3–20 μ W over the measured spectral range.

In Fig. 1, the extinction spectra of thin films of ZnPc on glass can be seen as well as the photoluminescence and photoluminescence excitation spectra of thin nanoparticle films. The absorption spectrum of the evaporated film of ZnPc (solid line) measured against a clean glass slide as reference shows a strongly broadened Q-band in the red and near infrared part of the spectrum. This is due to a π – π interaction of the ZnPc molecules in a close packed film that leads to a Davydov splitting and broadening of the absorption peak. The antireflection effect of the thin ZnPc film on the glass slide leads to the negative values for the extinction around 470 nm.

The nanoparticle films (dashed line) show a very strong and narrow luminescence centered at 605 nm with a photoluminescence excitation spectrum extending in the blue region of the spectrum. Noticeable is the strong overlap of the nanoparticle luminescence with the ZnPc absorption, a prerequisite for efficient resonant energy transfer. The nanoparticle films can be efficiently excited in the range of low absorption of the ZnPc, as can be seen in the photoluminescence excitation spectra of the nanoparticles.

In order to quantify the possible resonant energy transfer interaction between the molecules, a quenching experiment was performed in dilute solution. The photoluminescence of a nanoparticle solution was monitored during the stepwise addition of small amounts of ZnPc. A linear increase of the inverse luminescence intensity change on the molar concentration of the ZnPc is observed (Fig. 2b), indicating quenching according to the Stern–Volmer for-

malism. The quenching rate k_q can be thus obtained via the gradient of the inverse luminescence intensity K_{sv} with the Stern–Volmer formula

$$K_{sv} = k_q \times \tau_F.$$

The resulting quenching rate constant calculates to around 10⁸ s, with the measured nanoparticle luminescence lifetime τ_F of about 7 ns (amplitude averaged) and a calculated nanoparticle molar mass of 75 \times 10³ g/mol. Therefore, an efficient quenching process has to be present in the system.

Thermally evaporated films of ZnPc, such as used in the fabrication of organic solar cells, show packing induced intermolecular π – π -interactions which strongly quench the ZnPc luminescence, as radiative transitions from the lower Davydov-level are forbidden. The weak luminescence of a 40 nm thick film of evaporated ZnPc is broadened and featureless, as can be seen in Fig. 2a (dashed line, magnified 10 \times). After the addition of nanoparticles to the film, the luminescence signal (solid line) of the ZnPc in the range of 800 nm increases by a factor of approximately 15, indicating a transfer of energy from the nanoparticles to the ZnPc. The nanoparticles show a much higher absorption at the excitation wavelength of 514 nm than the pure ZnPc layer. At the same time, the luminescence of the nanoparticles is considerably quenched as compared to a layer of similar thickness deposited on clean glass (dotted line, divided by 5). The increase of luminescence in the ZnPc-layer is a strong indication that there is a resonant energy transfer rather than charge transfer occurring between the ZnPc and the nanoparticles.

Another way of identifying and quantifying resonant energy transfer is to study the dependence of the donor luminescence quenching on the thickness of the insulating

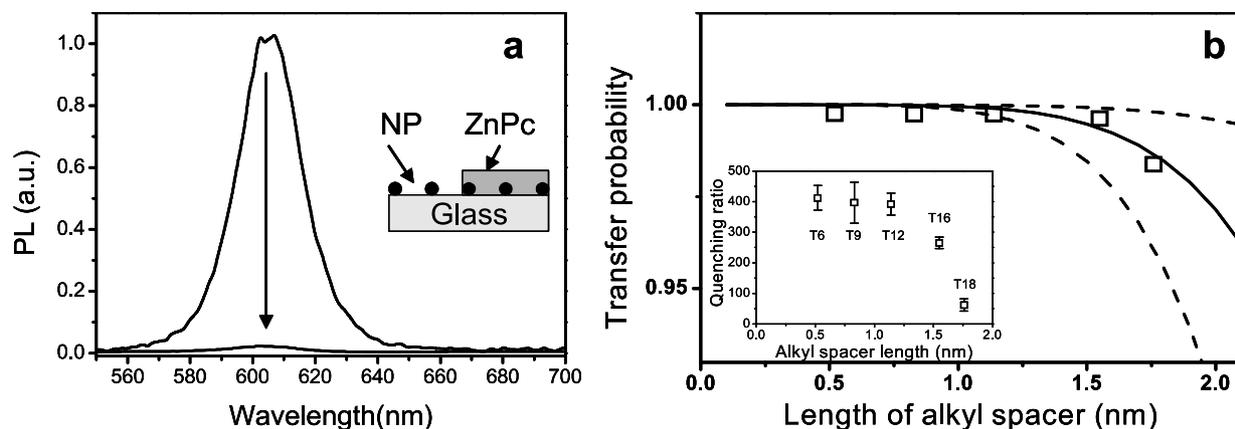


Fig. 3 **a** Photoluminescence spectrum of nanocrystals scattered on a glass slide before and after evaporation of a 20 nm thick layer of ZnPc. **b** Evolution of the transfer probability and the quenching ratio (*inset*) with different lengths of the ligand on the nanocrystal surface. The *lines* indicate different calculations according to Förster's theory with R_0 set to 3.6 nm (*solid line*) as well as 3 and 5 nm (*dashed lines*)

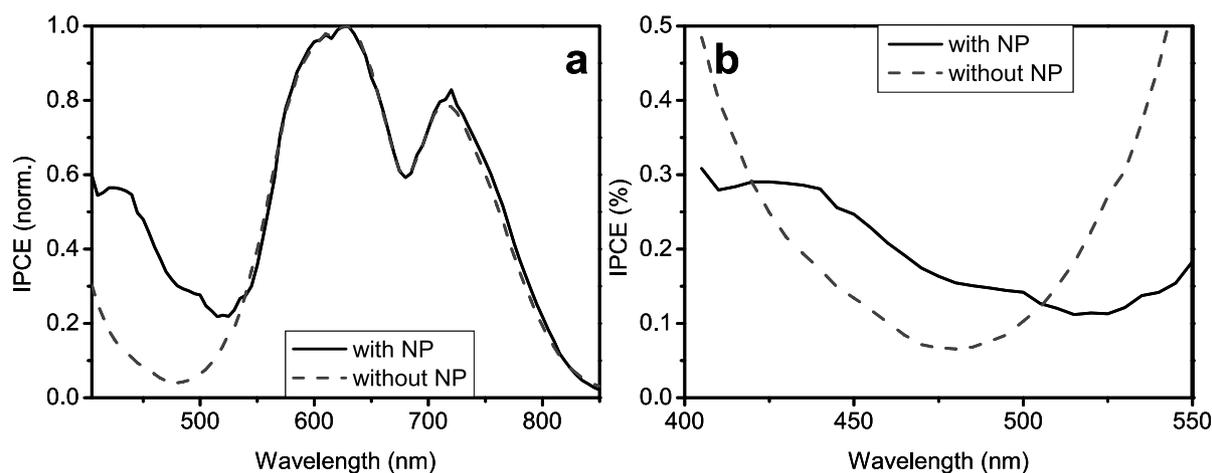


Fig. 4 **a** Normalized incident photon to converted electron efficiency spectrum of ZnPc photodiodes with (*solid line*) and without (*dashed line*) nanocrystals dropcast into the ZnPc layer. **b** Absolute values of IPCE in the spectral region of sensitization

shell between donor and acceptor matrix. For this reason, nanoparticles are scattered from dilute solution on a glass substrate with subsequent evaporation of ZnPc. Thus we can make sure that almost all of the nanoparticles are in close contact with ZnPc molecules held at a distance by the ligand shell. As expected, the nanoparticle luminescence is strongly quenched (Fig. 3a).

The inset of Fig. 3b shows the dependence of the nanoparticle luminescence quenching ratio on the length of the ligands covering the particles, assuming they are tightly packed and therefore fully elongated. 514 nm laser excitation leads to a strong photoluminescence signal of the nanoparticles which then is significantly quenched in the presence of ZnPc on top of the nanoparticles. As expected, the quenching ratio increases with smaller shell thickness, but saturates at spacer lengths of less than 1 nm. The quenching ratio is then over 400 : 1.

The donor–acceptor distance dependence of the energy transfer probability according to Förster's theory can be described by the following formula

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

R_0 , the so-called Förster radius, is the donor–acceptor distance at which the transfer probability is 50%. In well-tuned energy transfer systems it can reach values of around 5 nm.

Comparing calculations according to Förster's theory with the measured data, we can roughly estimate an effective Förster radius between 3 and 5 nm. Figure 3b shows the data points together with the calculated behaviour for a Förster radius of 3.6 nm (*solid line*, best fit) as well as 3.0 and 5.0 nm (*dashed lines*).

Charge transfer between the compounds therefore seems unlikely, because an overlap of the wavefunctions is required [16]; calculations show that in a model system of two conjugated polymers only at donor-acceptor distances much less than 1 nm efficient charge transfer can be expected [17].

Figure 4a shows the incident photon to electron conversion efficiency (IPCE) versus the wavelength of the incident light of a ZnPc photodiode with (solid line) and without (dashed line) nanocrystals deposited into the ZnPc layer normalized to the peak efficiency at 635 nm. The introduction of the nanoparticles into the active layer of the photodiode shows a distinct sensitization of the photocurrent generation in the spectral range of low ZnPc absorption around 500 nm. Above 580 nm, the nanoparticles do not absorb any light and the IPCE spectrum of both samples shows the same shape.

The absolute values of the IPCE shown in Fig. 4b indicate that the overall conversion efficiency is decreasing, most probably due to the hindered transport in the ZnPc film with interspersed nanocrystals. Around 500 nm though, a significant increase of the absolute quantum efficiency values can be observed due to the absorption of the nanocrystals with subsequent energy transfer to the ZnPc. The difference between the conversion spectra of photodiodes with and without nanoparticles resembles the nanoparticle excitation spectrum plotted in Fig. 1, with a decrease in the area of strong absorption in the ZnPc. There, a competition takes place between the absorption in the ZnPc and direct charge generation and the absorption in

the nanoparticles and subsequent energy transfer. The second process is less efficient, as it only introduces a further step. So an enhancement of the conversion efficiency can only be expected where the absorption in the nanoparticle layer significantly exceeds the absorption in the ZnPc layer.

We investigate the photophysical interactions between zinc-phthalocyanine and CdSe/ZnS nanocrystals. Photoluminescence measurements on thin ZnPc films with and without added nanocrystals indicate that resonant energy transfer is taking place. Further quantification of the resonant energy transfer is performed by changing the thickness of the shell of organic ligands around the nanoparticles. The luminescence is quenched very efficiently even with a nearly 2 nm thick shell. This indicates long range resonant energy transfer as quenching mechanism. We conclude that for photon harvesting purposes, usual ligand shell thicknesses between 1 and 2 nm will not reduce the efficiency of the energy transfer to the matrix significantly.

ZnPc photodiodes show a significant change of the IPCE spectrum upon addition of nanocrystals into the active layer. An increase of the quantum efficiency in the range of 500 nm is observed where there is a low absorption of the ZnPc but a strong absorption of the nanoparticles. Further work will have to be put in the device design to allow the nanoscale integration of the photon harvesting structure without deterioration of the charge transport processes [18].

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