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Buczynska, D.; Bujak, L.; Loi, Maria; Brotosudarmo, T. H. P.; Cogdell, R.; Mackowski, S.; Bujak, Ł.

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Energy transfer from conjugated polymer to bacterial light-harvesting complex

D. Buczynska,[1] Ł. Bujak,[1] M. A. Loi,[2] T. H. P. Brotosudarmo,[3,4] R. Cogdell,[3] and S. Mackowski[1,a)]

[1]*Optics of Hybrid Nanostructures Group, Institute of Physics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

[2]*Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands*

[3]*Ma Chung Research Center for Photosynthetic Pigments (MRCPP), Ma Chung University, Malang 65151, Indonesia*

[4]*Institute of Molecular Biology, University of Glasgow, Glasgow G12 8TA, United Kingdom*

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Energy transfer from a conjugated polymer blend (poly(9,9-dioctylfluorenyl-2,7-diyl):poly (2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene) to a light-harvesting complex 2 from purple bacteria has been demonstrated using time-resolved fluorescence spectroscopy. For our hybrid nanostructure, we observe a 30% reduction of the fluorescence lifetime of the polymer emission as compared to the pure polymer layer. This result is an important step towards integrating naturally evolved biomolecules with synthetic materials into biohybrid organic electronic systems. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4764082]

Photosynthetic complexes that evolved as a result of acclimation to environmental and light conditions are frequently highly selective over the spectral range at which this absorbs light. Leaves in higher plants absorb predominantly around 400 nm and 650 nm, as their main pigment is chlorophyll *a*.[1] In spite of this selectivity, light-harvesting complexes, which are well organized pigment assemblies fixed by a protein scaffold, provide excellent biological and biochemical functions for integration into artificial devices.[2] Among recent achievements in this field are assembling photosystems on metallic and semiconducting surfaces,[3,4] observation of the strong influence of plasmon excitations in metallic nanoparticles upon the absorption of the light-harvesting complexes,[5–9] and predicted plasmon enhanced photocurrent generation from photosystems.[10] On the other hand, there is a well established and growing interest in devices based on conjugated polymers that hold great potential for improving the efficiency of solar cells, light sources, etc.[11,12] In particular, the strong broad absorption of conjugated polymers makes them excellent candidates for improving the absorption efficiency of the light-harvesting complexes. In contrast to semiconductor quantum dots that have been recently applied as donors,[13] polymers are less toxic, their technology is well-developed and they require no surface modification.

In this work, a hybrid nanostructure composed of poly (9,9-dioctylfluorenyl-2,7-diyl):poly (2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene (PFO/MEH-PPV) conjugated polymer and the light-harvesting 2 (LH2) complex from purple bacteria is assembled for which the energy transfer from the polymer to the light-harvesting complex can be demonstrated. We consider this result as a major step towards integrating biologically functional molecules into organic photovoltaics and electronics. Such structures can be potentially used in an analogous way as photosynthetic complexes coupled to metallic nanoparticles, where plasmon excitations lead to increase of absorption at given wavelengths. In the case of hybrid nanostructures studied in this work, absorption of the naturally evolved functional photosynthetic complexes is broadened due to the energy transfer from the polymer layer, therefore, matching better the sunlight spectrum.

The LH2 complexes used in this experiment were isolated from purple bacteria *Rhodopseudomonas palustris*. A single LH2 complex contains 9 carotenoids and 27 bacteriochlorophyll *a* (BChl *a*) molecules, which are arranged in two rings: B800 and B850.[14] The absorption and emission spectra of the LH2 in buffer solution are shown in Fig. 1. The most pronounced bands observed at 800 nm and 850 nm originate from the B800 and B850 rings, respectively. BChl *a* also absorbs at 585 nm, while carotenoid absorption bands span from 400 nm to 550 nm. This broad absorption spectrum due to large number of pigments comprising the LH2 complex makes this biomolecule highly attractive for

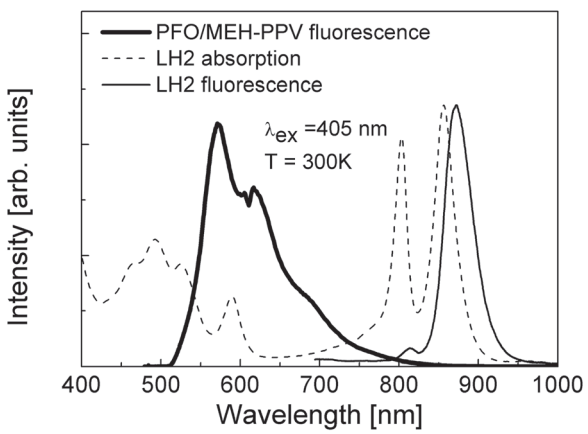

FIG. 1. Absorption (dashed line) and fluorescence (solid line) spectrum of the LH2 complexes from *R. palustris* together with the emission of the PFO/MEH-PP polymer blend.

a)Author to whom correspondence should be addressed. Electronic mail: mackowski@fizyka.umk.pl.

assembling hybrid nanostructures featuring energy transfer. The emission of the polymer blend PFO/MEH-PPV is very broad, as shown in Fig. 1, ranging from 500 nm to 800 nm. Importantly, the emission of the PFO:MEH-PPV features negligible overlap with the emission of the LH2 complex itself, also displayed in Fig. 1. The emission of the LH2 complex at 870 nm is associated with the strongly coupled B850 ring of BChl *a* molecules. We also observe a small emission band at 810 nm, which we tentatively ascribe to the emission of the B800 ring of BChl *a*. Comparison of the emission spectrum of the PFO/MEH-PPV polymer and the absorption of the LH2 complex shows moderate spectral overlap. However, there are also spectral ranges, where the polymer shows emission but the LH2 complex features negligible absorption (around 660 nm, for instance). In the latter region, energy transfer should be minimal.

There are essentially two important factors that determine the efficiency of the energy transfer between two nanostructures: the proximity between them as well as the spectral overlap between the emission of the donor and the absorption of the acceptor.[15] In the case of energy transfer between a single donor and a single acceptor, their respective orientation that defines the directions of transition dipole moments also plays crucial role. However, in the case of experiments carried out on highly concentrated samples, the dipole moments are randomly oriented. As shown in Fig. 1, the spectral properties of the components of the hybrid nanostructure studied in this work fulfill the prerequisite of spectral overlap between the emission of the donor (PFO/MEH-PPV) and the absorption of the acceptor. In order to assure close proximity between donors and acceptors, the hybrid nanostructure was fabricated in a layered geometry.

The layer of PFO/MEH-PPV on glass substrate was fabricated as described previously.[16] After polymer deposition, the substrates were stored in vacuum in order to minimize the effects of oxidation that leads to degradation of the optical properties of the polymer layer. To deposit the LH2 complexes, the substrate was removed from vacuum in darkness and a droplet (20 μl) of the LH2 complex solution in detergent was pipetted onto it. Next, after approximately half an hour, the sample was placed in a vacuum chamber and evacuated. The advantage of such a procedure is that the LH2 complexes after evaporation of the solvent are located directly on top of the polymer layer. However, this process of gradual evaporation also leads to inhomogeneity of the LH2 concentration at the surface. All optical experiments were carried out in such conditions on the same day the sample was prepared. With the hybrid nanostructures placed under vacuum conditions, we observed minimal degradation of the optical properties of both polymer and the LH2 complexes for about a week.

Fluorescence spectra of LH2 deposited on PFO/MEH-PPV polymer layer were measured in an optical setup in a backscattering geometry.[17] For excitation, a diode-pumped solid state laser with emission wavelength 405 nm and operated either in a continuous-wave or pulsed mode (BDL-405-SMC, Becker &Hickl) was used. The laser beam was focused on the sample surface to a spot with approximately 2 μm in diameter using a microscope objective 50×, 0.5 NA (Olympus) with the excitation power set to 1.3 μW. Spectrally resolved detection of fluorescence spectra was performed using an Amici prism coupled with a charge coupled device detector (iDus 420BV, Andor). Fluorescence lifetimes were measured using a time-correlated single photon counting method with a time correlated single photon counting (TCSPC) module (SPC-150, Becker &Hickl). The repetition rate of the laser was set at 20 MHz and the signal was detected with a fast avalanche photodiode (id100-50, idQuantique). In order to investigate spectrally different regimes, we monitored emission of the polymer with a band pass filter 550/10 (where there is spectral overlap between polymer emission and LH2 absorption) and with a band pass filter 670/10 (where the spectral overlap is very little). In order to account for possible inhomogeneities of the LH2 concentration, as well as possible roughness of the polymer layer, the fluorescence spectra were measured at 10 locations across the sample, while fluorescence decays were collected at 20 locations across the sample surface.

In Fig. 2, the fluorescence spectra acquired for ten different spots across the hybrid nanostructure composed of PFO/MEH-PPV and LH2 are shown. Contribution of the both constituents varies considerably from one spectrum to another and we attribute these differences to the inhomogeneity of the structure. Nevertheless, all the spectra feature strong contribution of the polymer emission and weak band at 870 nm that originates from the light-harvesting complex. The intensity scale for the low energy part of the spectrum was expanded tenfold in order to display the emission of the light-harvesting complexes. Much higher intensity of the polymer fluorescence results from larger extinction coefficients of the PFO/MEH-PPV at the excitation wavelength of 405 nm as compared to the LH2. Moreover, the fluorescence quantum yield of the polymer layer is almost 100%, whereas the quantum yield of the LH2 fluorescence is about 10%.[18] Generally, fluorescence spectra alone provide limited information regarding the possibility of the energy transfer between the polymer and the LH2 complexes.

The unambiguous way to demonstrate the energy transfer between donor and acceptor is to measure the fluorescence transient kinetics. In the presence of acceptors the fluorescence lifetime of the donors gets shorter. This reduction of fluorescence lifetime can be used to directly determine the

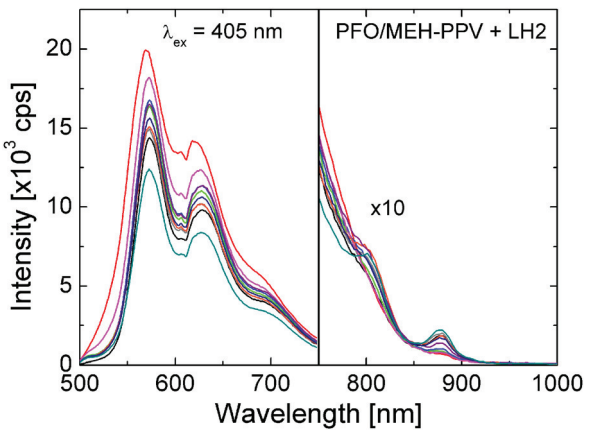

FIG. 2. Fluorescence spectra of LH2 deposited onto a layer of PFO/MEH-PPV polymer collected off ten different spots across the sample. The excitation wavelength was 405 nm. For wavelengths longer than 750 nm, the intensity was multiplied by 10.

efficiency of the energy transfer, in particular, any hybrid nanostructure.[15] In Fig. 3, representative fluorescence decay curves measured for our hybrid nanostructure at the detection energy of (a) 550 nm and (b) 670 nm are shown. These data are compared to the reference that is the pure polymer layer. The two chosen spectral regions correspond to substantially different regimes in regard to the LH2 absorption, which at 550 nm is substantially higher than at 670 nm. All measured fluorescence decays feature multiexponential behavior, typical of the polymer's fluorescence.[16] As can be seen in Fig. 3, in the case of 550 nm detection, a shortening of the fluorescence decay for the polymer covered with the LH2 complexes is observed. In contrast, the decays measured at 670 nm detection are identical for the hybrid nanostructure and the reference. The fluorescence decays were evaluated for 20 spots across the structure in order to obtain statistically significant information regarding the influence of the presence of the LH2 complexes upon the excitation dynamics in the PFO/MEH-PPV polymer. The results are summarized in Fig. 4 in the form of histograms for the same detection wavelengths as used previously. The decay times were determined at intervals where the fluorescence intensity drops by a factor of 1/3, the results are, however, insensitive to the particular choice of analysis of the transients. In the case of the 550 nm detection, the average fluorescence decay time is 0.55 ns and it is shortened by 25% in the case of the hybrid nanostructure, reaching the average value of 0.42 ns. We interpret the shortening of the fluorescence lifetime as a signature of the efficient nonradiative energy transfer from the polymer layer to the light-harvesting complex. The efficiency of the energy transfer for this wavelength range is equal to 25%. In contrast, for the 670 nm detection, the average fluorescence decay times were (0.55 ± 0.02) ns for polymer with LH2 and (0.55 ± 0.01) ns for the polymer alone. Therefore, we observe no change in the fluorescence transient behavior for this wavelength range. The origin of this difference presumably comes from very low absorption of the LH2 complex in this spectral range; therefore, there are no available states to which the energy transfer from the polymer could take place.

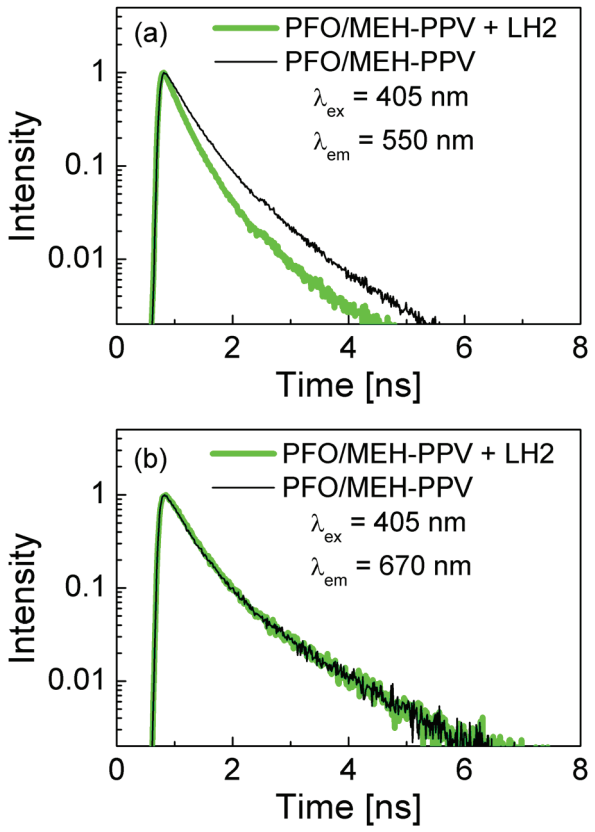

FIG. 3. Representative fluorescence decay curves measured for the hybrid nanostructure excited at 405 nm and detected at (a) 550 nm and (b) 670 nm. The data measured for the reference are also shown.

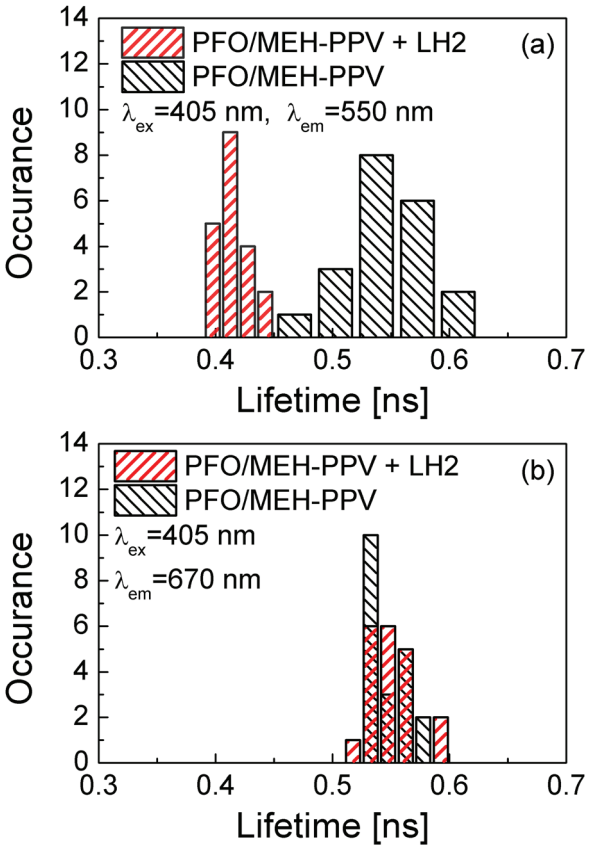

FIG. 4. Histograms of fluorescence lifetimes measured for the hybrid PFO/MEH-PPV polymer blend coupled to the LH2 complexes for detection wavelength of (a) 550 nm and (b) 670 nm. The results obtained for pure polymer are also shown. The excitation wavelength of 405 nm was used.

In conclusion, we demonstrate efficient energy transfer from the polymer layer to the light-harvesting complex. The efficiency of the energy transfer reaches 25% in the case where there is significant absorption of the light-harvesting complex. We consider this observation as a first step towards devising unique architectures based on assembling biomolecules with building blocks of the organic electronics in search for enhanced functionality.

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