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Energy transfer in hybrid organic/inorganic nanocomposites

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ABSTRACT

Chemically synthesized colloidal quantum dots can easily be incorporated into conjugated polymer host systems allowing for novel organic/inorganic hybrid materials combining the natural advantages from both organic as well as inorganic components into one system. In order to obtain tailored optoelectronic properties a profound knowledge of the fundamental electronic energy transfer processes between the inorganic and organic parts is necessary. Previous studies have attributed the observed efficient energy transfer to a dipole-dipole coupling with Förster-radii of about 50-70 Å. Here, we report on resonant energy transfer of non-equilibrium excitons in an amorphous polyfluorene donor CdSe/ZnS core-shell nanocrystal acceptor system. By time-resolved photoluminescence (PL) spectroscopy we have investigated the PL decay behavior of the primarily excited polyfluorene as a function of temperature. We show that the transfer efficiency drops from about 30% at room temperature to around 5% at low temperature. These results shed light on the importance of temperature-activated exciton diffusion in the energy transfer process. As a consequence the exciton has to migrate very close to the surface of the quantum dot in order to accomplish the coupling. Hence, the coupling strength is much weaker than anticipated in previous work and requires treatment beyond Förster theory.

Keywords: conjugated polymer, colloidal quantum dot, energy transfer, exciton diffusion

1. INTRODUCTION

Combining semiconductor quantum dots (QD) with π -conjugated organic materials represents a powerful way to create functional materials with optical and electronic properties not observed in neither of the source materials. Hybrid organic/inorganic nanocomposites have recently attracted considerable interest due to their promising optoelectronic properties. Blends of conjugated polymers and colloidal semiconductor quantum dots have been advantageously used for light-emitting diodes,^[1-3] ultra-sensitive radiation detection,^[4-6] and solar cells.^[7] The mechanism of charge separation at the polymer/semiconductor interface has been subject to intense studies.^[8-10] Besides the application driven interest, fundamental questions on the coupling between Frenkel excitons on organic molecules and Wannier excitons in inorganic semiconductors have gained enormous attention.^[11-14] Non-radiative energy transfer lies at the heart of many of the optoelectronic properties of these hybrid materials. While efficient transfer has been observed from conjugated polymers to colloidal semiconductor QD,^[15-17] surprisingly there is no excitation transfer from an organic dye attached via a protein to a QD.^[18]

The significant difference to the hybrid systems in Ref. 15-17 is the ability of exciton diffusion within the polymer host, whereas exciton diffusion along an aliphatic protein chain is almost impossible. Taking into account that exciton diffusion is a strongly temperature dependent process it should be possible to discriminate between pure incoherent electrostatic coupling and exciton diffusion.

Here, we report on detailed time-dependent photoluminescence (PL) investigations that focus on the intricate nature of the energy transfer between a conjugated polymer as donor and colloidal semiconductor QD as acceptor. Our organic/inorganic nanocomposite consists of CdSe/ZnS core-shell nanocrystals which are dispersed in an amorphous spin-coated poly[9.9-bis(2-ethylhexyl)fluorene-2.7-diyl] (PF2/6) film. In order to prevent aggregation of QD the concentration was set to 3% by weight. After initial optical excitation of the PF2/6, the excitation can be transferred from the PF2/6 donor to the QD acceptor. Previous studies in comparable composites suggested non-radiative resonant dipole-dipole interaction (Förster transfer) to explain the observed efficient excitation transfer from the polymer to the QD at room temperature.^[15-17] They found Förster radii of $R_0 = 50-70$ Å,^[16,17] which correspond to the distance between donor and acceptor where 50% of the excitations are being transferred. In Förster theory the oscillator strengths of the optical transitions and the spectral overlap between donor emission and acceptor absorption largely determine the Förster radius.^[19] The very long-range coupling observed in [16,17] is surprising since the Förster transfer between two organic dyes or polymer subunits (chromophores) is characterized by typical Förster radii of $R_0 \sim 40$ Å,^[20] and the transition

dipole matrix element of an organic acceptor molecule (Frenkel exciton) is expected to be larger than the one of inorganic QD (Wannier exciton).

2. EXPERIMENT

2.1 Sample Preparation

Poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl] (PF2/6, see Figure 1a) was synthesized via a Yamamoto-type aryl-aryl-coupling of the respective dibromo monomers with an average molecular weight M_n of about 129000 corresponding to approximately 330 repeat units per chain. The CdSe/ZnS core-shell quantum dots (see Figure 1b) have core crystal diameters between approximately 3.3 and 5.8 nm and were purchased in toluene solution from Evident Technologies. We spin-coated hybrid nanocomposite films from a toluene solution with 3%wt of QD relative to the PF2/6 weight onto fused silica substrates. All blends of QD with different sizes were fabricated with the same 3%wt QD fraction and a film thickness of approximately 200 nm. For the measurement of the neat QD absorption spectrum, poly(methyl methacrylate) (PMMA) with 3%wt QD content was drop-cast and characterized with a PerkinElmer Lambda 900 UV/VIS/NIR spectrophotometer. The thickness was measured with a Dektak V200Si profiler.

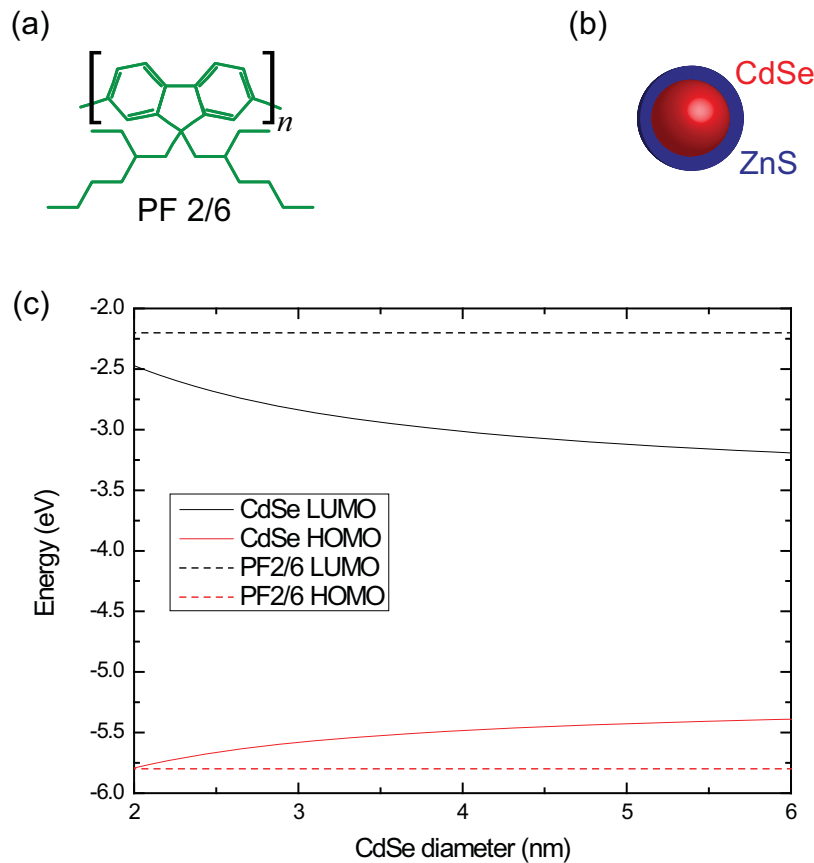


Figure 1: (a) Chemical structure of the monomer of the PF2/6. (b) Schematic structure of the quantum dot with a CdSe core and its surrounding ZnS shell. (c) Electronic band structure of the quantum dot acceptor and the polymer donor.

The electronic structure of the nanocomposite is shown in Figure 1c. The calculated^[27] highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the QD core is energetically within the HOMO-LUMO gap of PF2/6^[28] for all QD diameters (2.7 nm – 5.6 nm) used in the experiments.

2.2 Time-resolved measurements

The substrates with the PF2/6 nanocomposites were mounted in a liquid-helium flow cryostat with a helium exchange gas atmosphere. Optical pumping at 400 nm with pulses of <100 fs duration was performed by a frequency-doubled

Ti:Sapphire mode-locked oscillator with 80 MHz repetition rate. The photoluminescence was dispersed by a grating having 150 grooves/mm in a 300 mm spectrograph and detected using a Hamamatsu C5680 streak camera with 2 ps time-resolution. The time-resolved PL is measured with the streak camera system on the $S_1(v=0) \rightarrow S_0(v=1)$ transition of PF2/6.

2.3 Photoluminescence properties of the polymer

In Figure 2a we show the photoluminescence spectrum of PF2/6 at room temperature. The vibronic progression is clearly resolved. By slicing the spectrum in 2 nm wide bins, we extract the $1/e$ rise and decay times (Figure 2c and 2b, respectively) from the time-resolved photoluminescence spectrum as a function of wavelength. This reveals energetic relaxation of the excitations within the polymer at low temperature: While the decay time is shortened on the blue side of each peak of the vibronic progression, it is prolonged on the red side. Also the rise time on the red side is longer compared to the blue side. The reason for this well-known behavior is the inhomogeneous distribution of the density of states (DOS) which is due to the intrinsic energetic disorder in the amorphous polymer film originating from the statistical length variation of the subunits. After optical pumping the created exciton relaxes to energetically lower states by spatial migration. Jumps upwards in energy can occur because of temperature-activated hopping. For the subsequent analysis of the energy transfer in the nanocomposite, a spectral window around the PL peak of the $S_1(v=0) \rightarrow S_0(v=1)$ transition is integrated, as indicated in Figure 2.

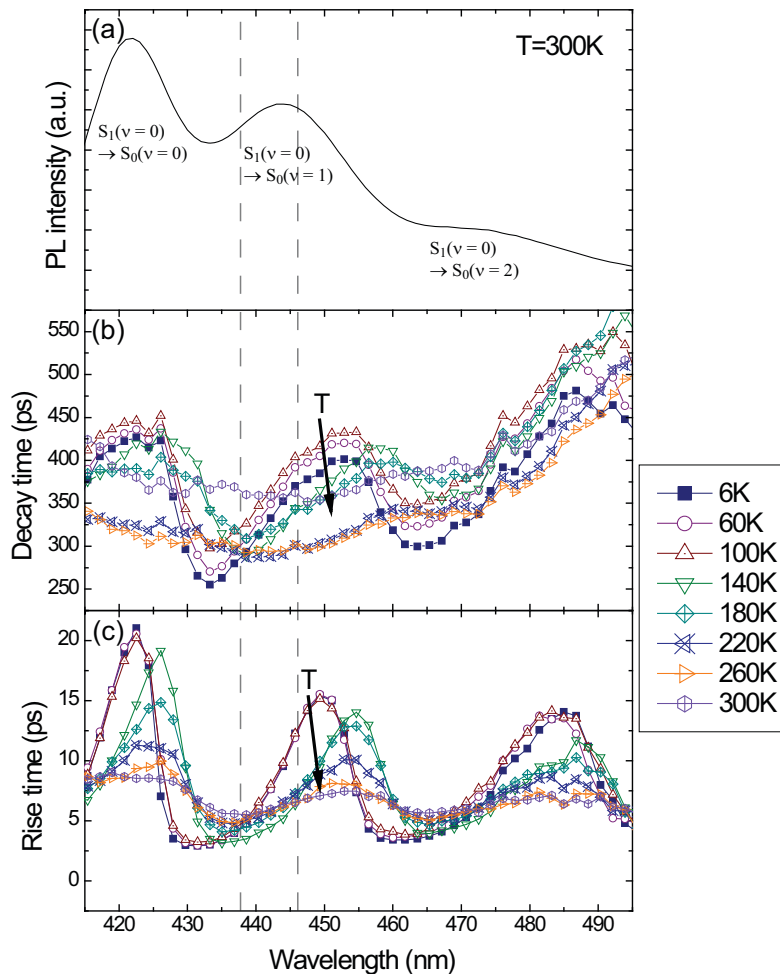


Figure 2: Photoluminescence (PL) spectrum of PF2/6 at room temperature. (b) Spectrally resolved PL decay time of the neat PF2/6 film for different temperatures. (c) PL rise time of PF2/6 as a function of wavelength and temperature. The dashed vertical lines indicate the spectral window which is integrated in order to obtain the time constants for the subsequent analysis of the energy transfer.

2.4 Excitation transfer to the QD acceptor

An exciton may either decay on the donor polymer by photoluminescence (PL) or non-radiative processes, or when a QD is sufficiently close, the energy can be transferred non-radiatively. Effectively this quenches the PL emission of the polymer and can therefore be monitored by time-resolved PL spectroscopy. The PL spectrum of PF2/6 and the absorption spectrum of the CdSe/ZnS QD exhibit the required large spectral overlap for an efficient non-radiative energy transfer (see Figure 4).^[17]

The efficiency of the transfer $Q = 1 - \tau_D/\tau_0$ is determined from the reduction in the $1/e$ decay time τ_D of the polymer/QD donor/acceptor system compared to τ_0 of the neat film without QD. For a known R_0 the efficiency can be estimated from the expression $Q = R_0^6/(d^6 + R_0^6)$ where d denotes to the donor-acceptor distance. At room temperature the observed transfer efficiency reaches up to 30% which is congruent with a large R_0 . However, when lowering the temperature to $T = 6$ K a decrease in the transfer efficiency to about 5% (see Figure 3) is observed. The spectral overlap of donor and acceptor does not change accordingly because the optical transitions are broadened by temperature-related dephasing effects, yet the underlying dipole matrix elements are mostly independent of temperature. Furthermore, the quantum efficiency of PF2/6 increases with lower temperature due to a decrease of non-radiating relaxation channels, from which higher transfer efficiency would be expected. As shown in Figure 3, the drop in transfer efficiency is quite independent of the center and width of the spectral window from which the time-resolved PL is analyzed.

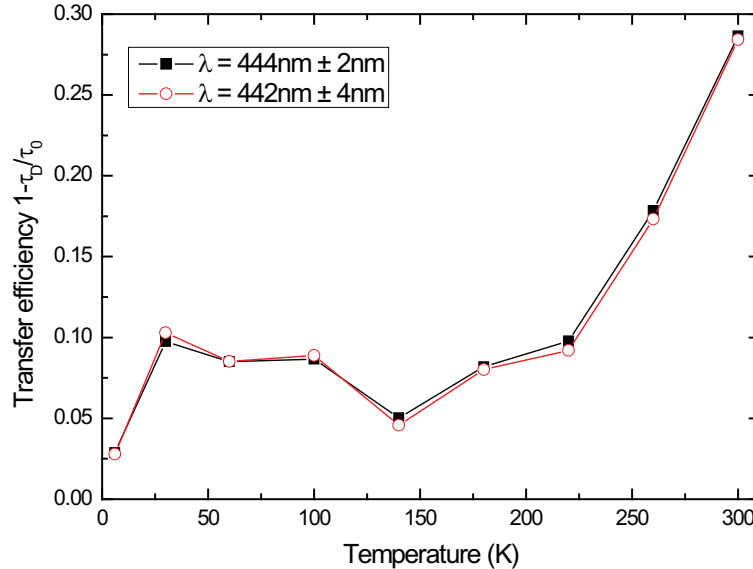


Figure 3: Transfer efficiency as a function of temperature for two different spectral windows from which the data is used.

2.5 Changing the spectral overlap between donor and acceptor

By using QD of different sizes we can change the spectral overlap between the donor PL and the acceptor absorption, see Figure 4. However, the observed temperature-dependent decrease in the excitation energy transfer efficiency appears independent of the QD center wavelength λ_c and hence the QD size. As shown in Figure 5 the maximum transfer efficiency at room-temperature decreases with QD size. This suggests that the non-radiative coupling may be reduced due to the smaller dipole coupling or less surface area of the QD for wavefunction overlap. The effect is even more pronounced considering that the QD doping fraction is constant by weight, i.e. the density of the smallest QDs ($\lambda_c = 530\text{nm}$) in the polymer is almost an order of magnitude higher than for the sample with the largest QDs ($\lambda_c = 620\text{nm}$).

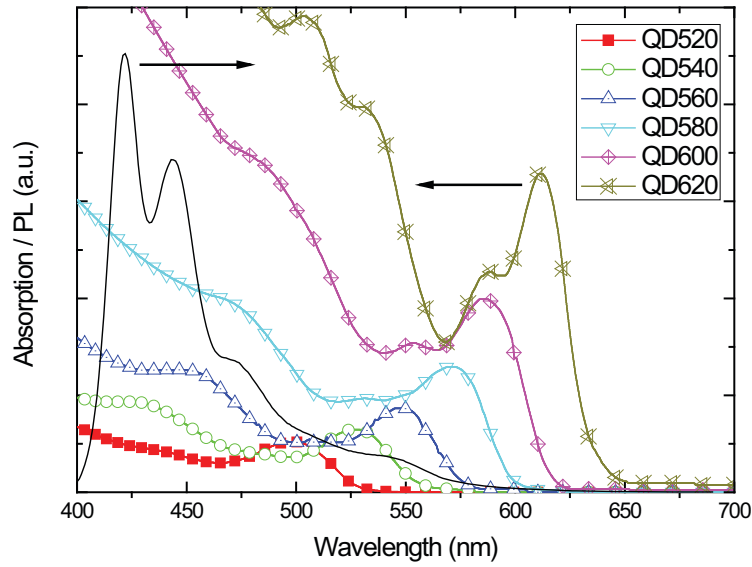


Figure 4: Room temperature photoluminescence spectrum of the PF2/6 donor and absorption spectrum of QD with different size. Not only the center wavelength changes with QD radius, also the lower extinction on the excitonic resonance^[26] reduces the spectral overlap with the donor for smaller QDs. Note that the QDs for this measurement are from a different fabrication batch than the ones which were studied by time-resolved PL.

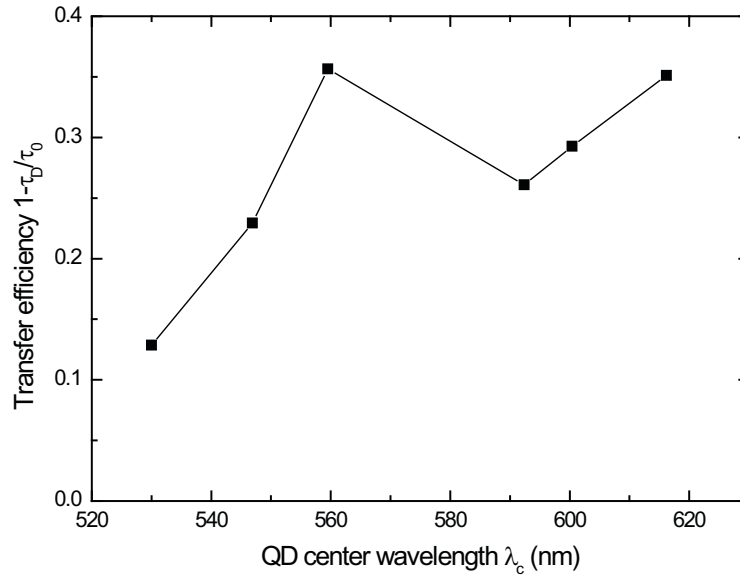


Figure 5: Room-temperature excitation transfer efficiency from time-resolved measurements as a function of QD center wavelength.

3. ENERGY TRANSFER MODEL INCLUDING EXCITON DIFFUSION

Taking the above mentioned findings into account, the decrease in transfer efficiency by lowering the temperature is surprising. On the other hand it is well-known that temperature-activated excitation energy migration occurs in conjugated polymers,^[21,22] and has a profound influence on the energy transfer from the amorphous polymer donor to randomly distributed acceptor dye molecules.^[23,24] The Yokota-Tanimoto model quantitatively describes the influence of diffusive exciton motion on the energy transfer process.^[25] The donor luminescence $I_D(t)$ as a function of time t exhibits a Kohlrausch-Williams-Watts behavior of a stretched exponential.^[24,25]

$$\begin{aligned}
I_D(t) &= I_D(t=0) e^{-\frac{t}{\tau_0}} \exp\left(-2B\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right), \\
B &= \left(\frac{1+10.87x+15.5x^2}{1+8.743x}\right)^{3/4}, \\
x &= D\left(\frac{R_0^6}{\tau_0}\right)^{-1/3} t^{2/3}, \\
\gamma &= \frac{2}{3} \pi^{3/2} R_0^3 c_A.
\end{aligned} \tag{1}$$

Here D denotes the diffusion coefficient and c_A the acceptor concentration. By fitting the measured PL decays with equation (1) we obtain R_0 and D . Since the exciton diffusion is a property of the polymer and is independent of the acceptor QD size, we simultaneously fit the data sets of all of the studied QD sizes with the same temperature dependent $D(T)$ but different R_0 . Because of the strong interdependency of the fitting parameters D and R_0 we fix $D(T = 300 \text{ K}) = 1.44 \text{ nm}^2\text{ps}^{-1}$, using this value from the literature as reference point.^[23] Figure 6 shows the deduced exciton diffusion coefficient as a function of reciprocal temperature. The temperature-activated diffusive exciton motion in amorphous conjugated polymers justifies an Arrhenius fit to the data. The resulting activation energy of 90 meV agrees well with the inhomogeneous width of the energy distribution in the amorphous polyfluorene film.^[22] Notably D decreases to a small but finite value around $D = 0.15 \text{ nm}^2\text{ps}^{-1}$ for temperatures below 150 K which can be explained by the energetic relaxation within the density of states towards energetically lower lying states. This process does not require thermal activation, and some exciton migration is retained even at zero temperature. On the other hand, due to the large spatial separation of the QD, the probability for an exciton to be transferred in close proximity to a QD by downward hops only is strongly delimited. Therefore, we attribute the observed decrease in transfer efficiency to the spatially reduced energetic relaxation process.^[22]

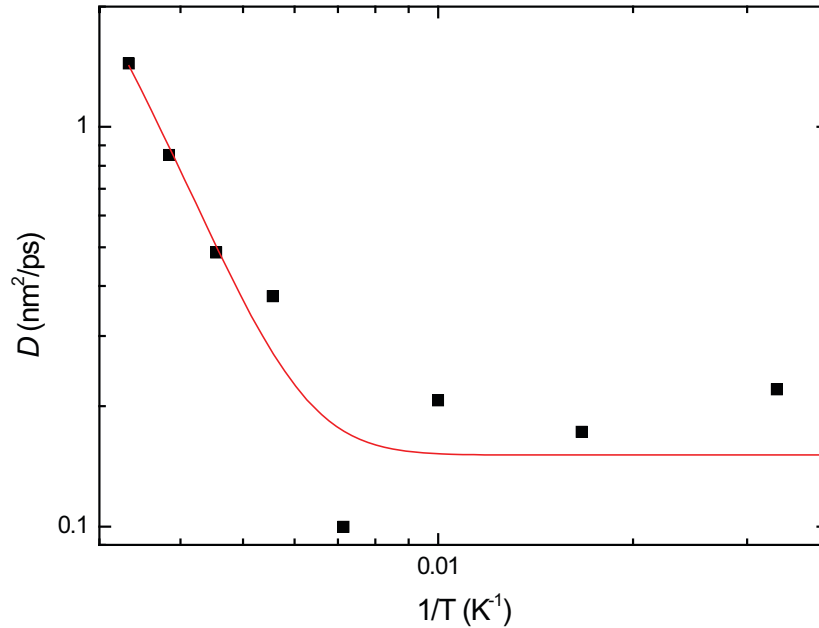


Figure 6: Temperature-dependent exciton diffusion coefficient deduced from a Yokota-Tanimoto model on the decay of the donor PL. The solid line is an Arrhenius fit to the data which confirms a temperature-activated hopping process.

Furthermore, by choosing QD of different sizes we vary the QD center wavelength and the spectral overlap between the PF2/6 emission and the QD absorption. Figure 7 shows the corresponding Förster radii R_0 calculated from Förster theory.^[19] However, fitting a Yokota-Tanimoto model (1) to time-resolved PL measurements at room temperature we find dramatically smaller transfer distances. Rather independent of the estimated QD size,^[26] the Förster radius is on the order of the respective CdSe nanocrystal radius including a monolayer ZnS shell. These characteristic transfer distances of 10-40 Å are significantly smaller than the 50-70 Å found in the literature from time-resolved PL measurements without considering exciton diffusion.^[16,17] In addition, the determination of the Förster radius from the spectral overlap overestimates the transfer distance by nearly an order of magnitude. Nevertheless, both models unambiguously show that the transfer radius decreases for smaller QD with shorter center wavelength. Effectively the exciton has to migrate to the surface of the QD prior to the non-radiative transfer. This reconciles the conflicting views in the literature on the possibility to convert a Frenkel exciton located at an organic molecule to a Wannier exciton,^[15-18] because in contrast to conjugated polymers,^[15-17] exciton migration is not possible along a protein chain.^[18] Since the length scales of the chromophores, the QD size and the Förster radius are comparable, a Dexter or multipole-multipole interaction is more appropriate than a dipole-dipole Förster-type interaction. Similar to the charge generation in QD-doped polymers for photovoltaics, the timescale of the energy transfer can be interpreted as diffusion time for an excitation in the polymer to reach the neighboring QD (transfer time of $\tau_{\text{transfer}} = 68$ ps at room temperature in Ref. [17]). However, because the transfer time and the timescale of the increase in the QD PL match,^[17] quenching of the PF2/6 PL due to charge separation at the polymer/QD interface can be safely excluded.

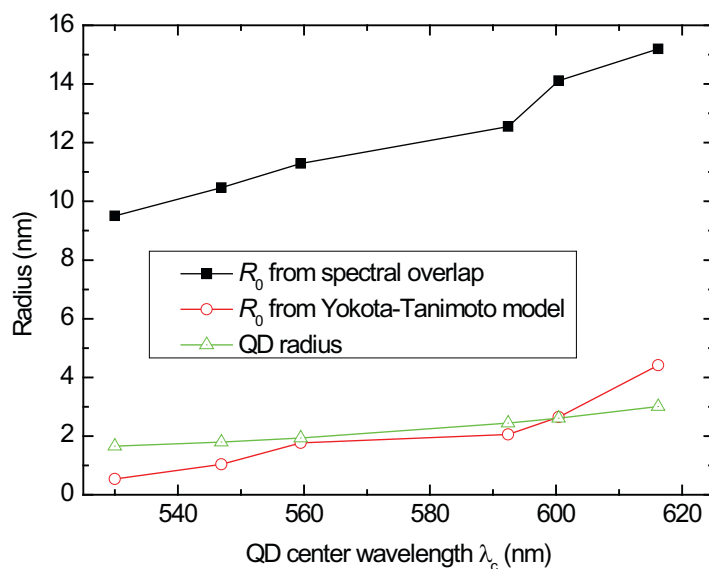


Figure 7: Comparison of the Förster radius R_0 obtained from the spectral overlap of the donor emission and the acceptor absorption and the values from the Yokota-Tanimoto model that was fitted to the measured decay of the donor PL. The latter one takes into account exciton diffusion which leads to a characteristic transfer radius on the order of the calculated QD radius.

4. CONCLUSIONS

In conclusion, our experimental findings shed light onto the central question about the incoherent radiationless coupling between the electronic states of the donor and the acceptor in such hybrid systems. We show that the radiationless coupling between the polymer and the QD is way beyond the simple dipole – dipole coupling approach thus contradicting conclusions about the transfer distances (and therefore the transfer efficiency) as reported in Ref. 16 & 17.

In order to harness the full potential of hybrid organic/inorganic nanocomposites in many fields of application a detailed microscopic understanding of the energy transfer process will allow further optimization of the optoelectronic properties. Still the creation of hybrid Frenkel/Wannier excitons remains a tantalizing fundamental challenge.

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