

# Excitonic energy transfer dynamics in hybrid organic/inorganic nanocomposites at high loading levels

Burak Guzelturk<sup>1</sup>, Pedro-Ludwig Hernandez Martinez<sup>1</sup>, Donus Tuncel<sup>1</sup>, and Hilmi Volkan Demir<sup>1,2</sup>

<sup>1</sup>Department of Electrical and Electronics Engineering, Department of Physics, and UNAM - Institute of Materials Science and Nanotechnology Bilkent University, Ankara, Turkey TR-06800

<sup>2</sup>School of Electrical and Electronics Engineering, School of Physical and Mathematical Sciences, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

Email: [volkan@bilkent.edu.tr](mailto:volkan@bilkent.edu.tr) and [hvdemir@ntu.edu.sg](mailto:hvdemir@ntu.edu.sg)

**Abstract:** Temperature dependent exciton migration in the hybrid nanocomposites of conjugated polymers chemically integrated with quantum dots is studied at high loading levels. The underlying interplay between the exciton transfer and diffusion is revealed.

**OCIS codes:** (260.2160) Energy transfer; (160.4236) Nanomaterials; (160.4760) Optical properties

Colloidal quantum dots (QDs), also known as semiconductor nanocrystals, find numerous important applications in optoelectronics thanks to their favorable optical properties. However, the assemblies of these QDs are generally known to possess poor electrical properties. This necessitates the use of additional material systems in conjunction with QDs including conjugated polymers to enhance their properties through hybridization. To exploit such hybrid organic/inorganic systems, however, the excitonic interactions are the key. To this end, developing a deeper understanding of the excitonic processes (e.g., exciton diffusion and transfer) in these hybrid systems is essential.

Efficient exciton injection in the hybrid systems of conjugated polymer-QD nanostructures is a scientific challenge due to several limitations. In the blended polymer-QD thin films, severe phase separation can occur, especially for increased QD loadings. As a result of the segregated constituents, excitonic interactions, such as Förster-type exciton transfer, are fundamentally limited, as they are very sensitive to the effective separation of the species at the nanoscale. Although phase-separated films can be used to advantage for other purposes, e.g., thin film device fabrication [1], efficient exciton transfer is not possible in plane across these partitioned hybrid structures.

The exciton diffusion in the polymers has been suggested to provide critical assistance for the nonradiative energy transfer (NRET) of excitons into the QDs in blended organic-inorganic nanostructures in a recent study, which was carried out at low QD loading levels (only up to 3w%). [2] Nevertheless, effects of the exciton diffusion at increased QD loadings have not yet been studied nor understood to date. Previously, Lutich *et al.* discussed the decreased exciton diffusion in a layer-by-layer constructed organic-inorganic hybrid system effectively for 19w% QD loading, but the fundamental reason of this decrease has not been clear. [3]

In this work, to address the problem of limited exciton injection in the polymer-QD hybrids, we propose and demonstrate an organic-inorganic nanocomposite system, where phase separation can be substantially reduced through the targeted specific interactions between the integrated species, making it possible to achieve high QD loadings. Consequently, unprecedented energy transfer efficiency is observed for increased QD loadings where Förster-type exciton transfer dominates the excitonic dynamics and the exciton diffusion is no longer critical. This model system allows for developing an understanding of the underpinning interplay between the exciton transfer and diffusion, which leads to either their cooperation (for low QD loading) or their competition (for high QD loading).

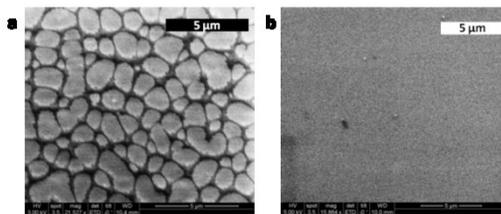


Fig.1. Scanning electron microscopy (SEM) images of hybrid organic-inorganic thin films made of (a) non-functionalized PF:QD blend and (b) functionalized PF:QD composite, both at the 45w% QD loading level. The scale bars are 5 $\mu$ m.

The proposed hybrid nanostructure consists of carboxyl acid moiety functionalized polyfluorene (PF) integrated with core/alloyed-shell CdSe/CdS/ZnS QDs, enabling reduced phase segregation in thin films by the specific functionalization of the polymer (see Fig. 1(b)). This hybridization is further verified via TEM, XPS and TGA measurements. Conversely, a non-functionalized PF is blended with the same QDs at the same loading level of 45w%, where severe phase segregation is clearly observed due to the absence of the specific interaction between the two species as shown in Fig. 1(a).

After resolving the problem of phase segregation, we studied the emission kinetics of the organic-inorganic nanocomposite of functionalized PF:QDs at various QD loading levels and showed that functionalized PF enables higher energy transfer efficiencies at increasing QD loadings, as compared to significantly lower efficiencies in non-functionalized PF-QD blends. Furthermore, using temperature dependent time-resolved fluorescence spectroscopy, we investigated the cooperative *vs.* competitive nature of the exciton diffusion in the polymer for NRET of the excitons into the QDs in the hybrid thin films at different QD loadings. As shown in Fig. 2(a), the energy transfer efficiency levels obtained for high QD loading (45w%) are substantially higher than those for low QD loading (3w%) especially at low temperatures. They also exhibit characteristically different trends with respect to the sample temperature. In the high loading case, the energy transfer efficiency is found to be less sensitive to the temperature, unlike the low QD loading case, where a temperature activated process is observed. To understand the underlying physics of this activation coming from the exciton diffusion, we employed a physical model to relate exciton diffusion to the QD loading, making use of an approach previously proposed by Gösele [3]. The model considers exciton diffusion in the organic material as an assisting process to the NRET, for which the resultant efficiency is derived as given in (1).

$$\eta = 1 - \frac{1}{1+4 D n_A \pi r_F \tau_D} + \frac{e^{\left[ \frac{\gamma_{DA}^2}{1+4 D n_A \pi r_F \tau_D} \right]} \sqrt{\pi} \gamma_{DA} \operatorname{erfc} \left( \frac{\gamma_{DA}}{\sqrt{1+4 D n_A \pi r_F \tau_D}} \right)}{(1+4 D n_A \pi r_F \tau_D)^{\frac{3}{2}}} \quad (1)$$

Here  $D$  is the diffusion coefficient,  $n_A$  is the QD density (number of QDs per unit volume),  $\gamma_{DA}$  is the reduced acceptor concentration dependent on  $n_A$  and Förster radius  $R_{0A}$ , and  $r_F$  depends on  $D$ ,  $R_{0A}$ , and the bare donor lifetime  $\tau_D$ . In Fig. 2(b) theoretically modeled efficiencies are presented in the form of iso-efficiency-curves as a function of  $D$  *vs.*  $n_A$  on the top and  $L_D$  (diffusion length) *vs.* center-to-center QD separation on the bottom, separately for low level of QD loading on the left and high level on the right.  $n_A$  and center-to-center QD separation are calculated within a margin known for these low and high QD loaded films based on the amount of materials used in the films. In Fig. 2(b) the corresponding margins for  $D$  and  $L_D$  are also shaded. For the low QD loading,  $D$  is estimated to be  $>1000$  nm<sup>2</sup>/ns and  $L_D$  is  $\sim 13$  nm at room temperature, which are comparable to the previously reported values [2]. However, significant modifications of  $D$  and  $L_D$  are observed in the case of high QD loading, where  $D$  is estimated  $\sim 150$  nm<sup>2</sup>/ns and  $L_D$  is  $<5$  nm. We conclude that the exciton diffusion is strongly suppressed at the high QD loading level. This suppression is mainly due to increased rates of NRET from the polymer to the QDs with smaller effective donor-acceptor separations at high QD loadings, and thus the resulting predominance of the exciton transfer in the competition with the diffusion process. This is supported by the energy transfer efficiencies being less temperature dependent for high QD loadings, indicating that the exciton diffusion assisting is not critical.

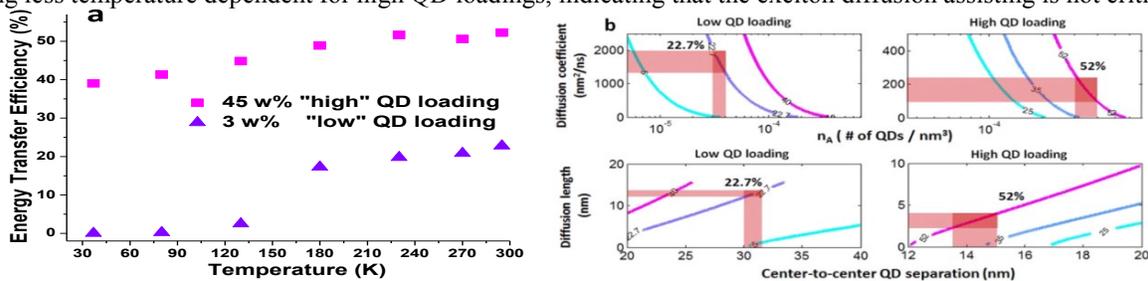


Fig. 2. (a) Temperature dependent energy transfer efficiencies for low and high QD loadings, and (b) room temperature iso-efficiency curves, top  $D$  *vs.*  $n_A$ , bottom  $L_D$  *vs.* center-to-center QD separation. Left for low QD loading, right for high QD loading.

To sum up, functionalized polymers, like PF derivatives in this model system, can suppress phase separation in their nanocomposite thin films to serve as efficient exciton donors for the integrated QDs. Theoretical modeling of the temperature dependent NRET dynamics reveals the interplay between the Förster-type exciton transfer and the exciton diffusion to be cooperative for low QD loadings and competitive for high QD loadings. Contrary to the common consideration that the exciton diffusion plays a critical role in the resulting excitonic dynamics of such polymer-QD nanocomposites, the experimental evidence and supporting theoretical model suggest that the exciton diffusion is not essential at high loading levels when the exciton transfer dominates.

This work is supported by NRF-RF-2009-09 and NRF-CRP-6-2010-2, and also by EU-FP7 Nanophotonics4Energy-NoE, and TUBITAK EEEAG 109E002, 109E004, 110E010, and 110E217. H.V.D. acknowledges support from ESF-EURYI and TUBA-GEBIP.

## References

- [1] S. Coe, W. Woo, M.G. Bawendi, V. Bulović, *Nature* **420**, 800-803 (2002).
- [2] T. Stöferle, U. Scherf, R.F. Mahrt, *Nano Lett.* **9**, 453-456 (2009).
- [3] A.A. Lutich, A. Pöschl, G. Jiang, F.D. Stefani, A.S. Susha, A.L. Rogach, J. Feldmann, *Appl. Phys. Lett.* **96**, 083109 (2010).
- [4] U. Gösele, M. Hauser, U.K.A. Klein, and R. Fray, *Chem. Phys. Lett.* **34**, 519-522 (1975).
- [5] B. Guzelurk, P.L. Hernandez, D. Tuncel, H.V. Demir (in submission).