

Theoretical study of excitonic energy transfer in carbon-nanotube-based photovoltaics

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Carbon nanotubes (CNTs) are quasi-one-dimensional materials with a very unique set of optical, electronic, and mechanical properties. Their tunable optical band-gap and high optical density have drawn the attention of researchers in the optics community. While a majority of research efforts have focused on understanding the photophysics of individual CNTs, understanding the coupling of CNTs to the surrounding environment and the nearby CNTs have shown to be of vital importance in understanding the photoexcitation dynamics in these systems [1].

Excited states of the electronic system in CNTs are the bound states between an electron in the conduction band and a hole in the valence band, known as excitons. The excitonic energy transfer (EET) from an initial CNT (donor) to a final CNT (acceptor) is the focus of this study. We show the unconventional behavior of the transfer rate with respect to chirality of the CNTs and their orientation. We also show, for the first time, that the excitons that cannot be excited by light (dark excitons) contribute significantly to the energy transfer process.

The excitonic states are best described by the Bethe-Salpeter equation (BSE). Here, we use the tight-binding single-particle wave functions as a basis to solve the BSE and calculate the excitonic eigenfunction and energies. The exciton states are divided into singlets and triplets according to spin, and can have symmetric or antisymmetric wave function over the relative coordinate. Among the four types of excitons, only the spin singlet and antisymmetric excitons are bright and the rest are dark [3].

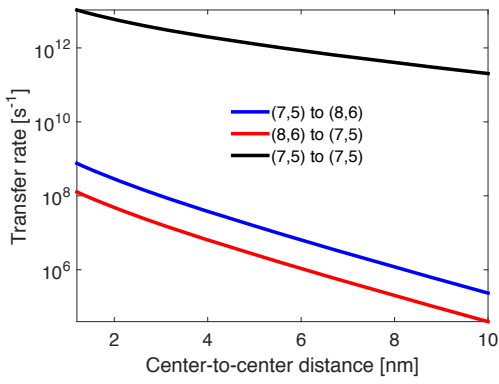
The EET rate is calculated by treating the Coulomb coupling between CNTs as a perturbation

in Fermi's golden rule. In the molecular aggregates where the sizes of molecules are small relative to the separation between them, the Coulomb interaction is effectively equal to the interaction between the transition dipoles of the molecules; this is known as the transition-dipole approximation (TDA). In the original work by Förster [2], it was shown that in this limit the EET rate is dependent on the overlap of the emission and absorption spectra of molecules, both of which depend on the bright excited states. However, our study shows the breakdown of this approximation from different aspects.

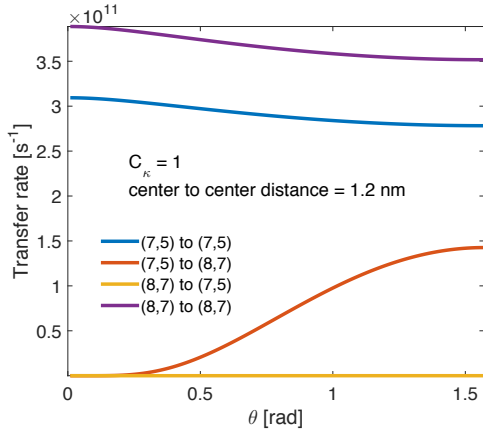
First, the EET rate has an exponential decay with increasing spacing between the donor and acceptor tubes, as opposed to the R^{-6} dependence calculated through the TDA (Figure 1a). Second, the EET rate is significant when the donor and acceptor tubes are perpendicular to each other (Figure 1b). This is in sharp contrast with the result of the TDA which predicts zero transfer rate at perpendicular orientation. Third, we show that, in addition to bright excitons, one type of dark exciton (singlet and symmetric) contributes to the EET due to the large size of the CNTs (Figures 1b and 1c). This is a nonintuitive result which underlines the non-radiative nature of the EET.

Furthermore, we show that the EET between similar chirality CNTs is about 3 orders of magnitude larger than the transfer rate between donor and acceptor CNTs with dissimilar chiralities (Figure 1a). This is due to the momentum conservation in the parallel orientation. The difference in the transfer rate rapidly diminishes with rotating the CNTs with respect to each other.

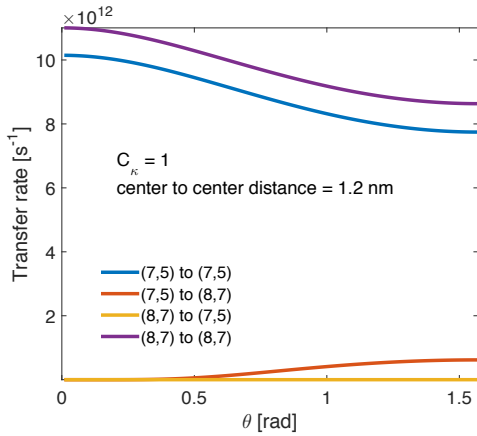
It has been shown that the environmental screening of the Coulomb interaction between electrons and holes changes the exciton energy dispersion



(a)



(b)



(c)

Fig. 1. (a) The EET rate of antisymmetric singlet excited states between parallel donor and acceptor CNTs of various chirality as a function of tube separation. (b) The EET rate of antisymmetric singlet excited states donor and acceptor CNTs of various chirality as a function of the relative orientation. (c) The EET rate of symmetric singlet excited states between donor and acceptor CNTs of various chirality as a function the relative orientation.

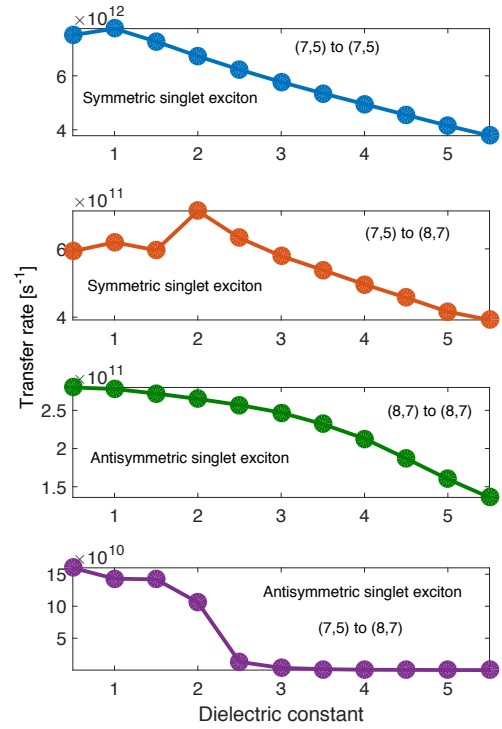


Fig. 2. The EET rate of symmetric and antisymmetric singlet excited states between donor and acceptor CNTs of various chirality as a function of environment dielectric constant.

curve, as well as the exciton wavefunction. Here, we show that the change is not uniform for CNTs with different chirality; As a result, the EET rate tends to decrease with increasing environment dielectric constant. This dependence is more pronounced for the bright exciton transfer process between CNTs of dissimilar chirality (Figure 2).

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