Förster-Induced Energy Transfer in Functionalized Graphene

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ABSTRACT: Carbon nanostructures are ideal substrates for functionalization with molecules since they consist of a single atomic layer giving rise to an extraordinary sensitivity to changes in their surrounding. The functionalization opens a new research field of hybrid nanostructures with tailored properties. Here, we present a microscopic view on the substrate–molecule interaction in the exemplary hybrid material consisting of graphene functionalized with perylene molecules. First experiments on similar systems have been recently realized illustrating an extremely efficient transfer of excitation energy from adsorbed molecules to the carbon substrate, a process with a large application potential for high-efficiency photovoltaic devices and biomedical imaging and sensing. So far, there has been no microscopically founded explanation for the observed energy transfer. Based on first-principle calculations, we have explicitly investigated the different transfer mechanisms revealing the crucial importance of Förster coupling. Due to the efficient Coulomb interaction in graphene, we obtain strong Förster rates in the range of 1/fs. We investigate its dependence on the substrate–molecule distance R and describe the impact of the momentum transfer q and describe the impact of the momentum transfer q.

The observed energy transfer could be explained by two major nonradiative energy transfer mechanisms (as depicted in Figure 1): (i) Förster27 and (b) Dexter28 energy transfer in perylene-functionalized graphene. The Dirac cone represents the electronic band structure of graphene, while the electronic states of the perylene molecules are described by a two-level (HOMO–LUMO) momentum independent system. The arrows in (a) show different energy-conserving processes involving varying momentum transfer q.

The continuing trend to miniaturization of devices in modern technology leads to fundamental physical limits of applied materials.1,2 The search for new materials and new functionalities brings hybrid systems into the focus of current research.3,4 They consist of low-dimensional nanostructures functionalized with single molecules combining the remarkable properties of both subsystems. In particular, carbon nanostructures are excellent substrates, since they offer a variety of metallic and semiconducting systems showing a large sensitivity to changes in their surrounding.5–9 Noncovalent functionalization based on π−π stacking preserves the intrinsic properties of the substrate to a large extent.10 At the same time, the interaction with the attached molecules induces additional properties desired for specific technological applications.11–19

First experiments have been realized illustrating the successful functionalization of carbon nanotubes with photoactive molecules suggesting the design of efficient carbon-based molecular switches.10,13,20–22 Recently, a strong excitation energy transfer has been observed in perylene- and porphyrin-functionalized carbon nanotubes suggesting efficient photodetection and light harvesting.23–25 First studies on functionalized graphene also reveal high energy transfer rates between the attached molecules and the graphene layer.26 The combination of unique transport properties of graphene, including ballistic transport and strong light absorption of organic molecules, results in new hybrid nanostructures with large application potential for high-efficiency photodetectors, biomedical sensors, and photovoltaic devices.26

Figure 1. Schematic illustration of the nonradiative (a) Förster27 and (b) Dexter28 energy transfer in perylene-functionalized graphene. The Dirac cone represents the electronic band structure of graphene, while the electronic states of the perylene molecules are described by a two-level (HOMO–LUMO) momentum independent system. The arrows in (a) show different energy-conserving processes involving varying momentum transfer q.
depends on the molecular transition dipole moment $\mathbf{d}$ and it exhibits a $R^{-4}$ dependence for hybrid nanostructures on top of a spatially extended two-dimensional substrate\textsuperscript{26,30} (in contrast to the well-known $R^{-6}$ scaling for dipolar Förster coupling in molecule–molecule complexes). (ii) Dexter coupling\textsuperscript{28} is based on a charge transfer between the molecule and graphene states, see Figure 1b. After the process, the molecule is brought into its ground state, and graphene becomes excited and can emit light through carrier recombination. It is a short-range transfer mechanism that directly depends on the spatial overlap of involved molecule and graphene orbital functions resulting in an exponential decay with the substrate–molecule distance $R$.

Recent studies indicate that the observed energy transfer in carbon-based hybrid nanostructures can probably be traced back to a Förster-like transfer process.\textsuperscript{26,31} In these studies, the molecule–substrate distance is clearly larger than 10 Å due to the presence of long nonconducting linker molecules. However, for functionalization procedures without such additional molecules, the distance is in the range of just a few Å corresponding to the van der Waals radius of the involved atoms.\textsuperscript{23,26,31} Here, the Dexter transfer mechanism is expected to be a competing energy transfer mechanism. In this Article, we present a systematic first-principle study on the substrate–molecule interaction in the exemplary hybrid system consisting of graphene functionalized with perylene molecules. The obtained insights should be applicable to other carbon-based hybrid nanostructures. We study the molecule-induced changes in the electronic band structure and the optical properties of graphene as well as the charge rearrangements within the two subsystems. Combining first-principle calculations characterizing the hybrid material with tight-binding-based calculations of the Förster transfer rate, we obtain an analytic expression allowing us to explicitly determine the strength of the Förster coupling. To address the question which transfer mechanism is likely to be responsible for the efficient energy transfer observed in experiments on carbon-based hybrid materials,\textsuperscript{23,26,31} we discuss the competing Dexter transfer mechanism by estimating the spatial overlap of the involved substrate and molecule orbitals within first-principle calculations.

The investigations are based on density functional theory (DFT) calculations performed within the FHI-aims code package.\textsuperscript{52} It is an all-electron, full-potential electronic structure code, including numerical atom-centered orbitals, which are very efficient allowing the investigation of structures containing hundreds of atoms. All calculations are done within the tight settings including a tier 2 basis set for the carbon and hydrogen atoms.\textsuperscript{52} Calculations with increased accuracy in the basis functions revealed that the chosen settings already lead to converged results with respect to the total energy. We focus on graphene functionalized with perylene molecules ($C_{20}H_{12}$), see Figure 2a,b, illustrating the top and side view of the studied structure. For graphene, we choose a supercell covering $7 \times 7$ unit cells corresponding to 98 carbon atoms, with a lattice constant of 1.42 Å. The investigated situation corresponds to a doping of graphene. The electron interactions are described within the PBE exchange-correlation functional,\textsuperscript{53} including the recently implemented van der Waals correction\textsuperscript{54} to account for the long-range van der Waals interaction. The latter plays a fundamental role in describing the weak molecule–nanostructure coupling that is of paramount importance to quantitative estimate the relative contribution of the Dexter transfer mechanism. We also performed additional calculations with the hybrid functional PBE0\textsuperscript{55} and HSE06\textsuperscript{56,37} to investigate the alignment of molecular levels. We found that the molecular HOMO (LUMO) level is located below (above) the Fermi energy in graphene and, thus, initial spurious charge transfer does not occur.

The initial perylene-functionalized graphene structure is fully relaxed using the Broyden–Fletcher–Goldfarb–Shanno method minimizing all force components to values smaller than $10^{-3}$ eV/Å. Figure 2a illustrates the hybrid nanostructure after geometric relaxation. The comparison with the perfectly flat graphene layer (orange color) reveals a slight dent of carbon atoms of less than 0.1 Å close to the molecule. This geometric distortion is a direct consequence of the presence of the perylene molecule and can be traced back to the Pauli repulsion.\textsuperscript{38,39} It also gives rise to a charge rearrangement, which will be discussed below.

We find an optimal substrate–molecule distance of $R_{\text{min}} = 3.25$ Å, which is slightly smaller than the initial value of the van der Waals diameter of the carbon atom, see Figure 2c. The optimal binding energy at $R_{\text{min}}$ is $E_b = -1.96$ eV corresponding to a binding energy of $E_b = -61$ meV per atom in the perylene molecule. This is in the expected range for a van der Waals-induced noncovalent adsorption of the molecule to the graphene surface. The $\pi$-electronic system of the perylene molecule is linked to the graphene surface via $\pi\rightarrow\pi$ stacking, which is much less invasive compared to the covalent adsorption.\textsuperscript{37} This can be well observed on the only minor changes in the electronic structure of the substrate, see Figure 3. Our calculations clearly illustrate that the unique band structure of graphene, including the Dirac point and the linear bands, is entirely preserved after the noncovalent functionalization with perylene molecules. The observable changes appear at the points where the molecular HOMO and LUMO levels cross the graphene electronic states, as illustrated in the inset of Figure 3. Here, the resulting states of the hybrid nanostructure exhibit avoided crossings. This well-known behavior in
quantum chemistry is further illustrated within the zoomed-in region around the molecular LUMO level, which anticrosses the graphene electronic states several times.

As a direct consequence of the almost completely preserved electronic band structure, the optical properties of graphene remain unchanged to a large extent, see Figure 4. The optical absorption of the hybrid nanostructure corresponds to an overlap of the absorption peaks of the pristine graphene and isolated perylene molecule, as shown in Figure 4a. The optical matrix element corresponding to the expectation value of the momentum operator $\langle \vec{p} \rangle = \langle \Phi | \vec{p} | \Phi \rangle$ exhibits only slight changes in the region, where avoided crossing takes place, see the blue-shaded circles in Figure 4b. Note, however, that the energy transfer within the hybrid nanostructure is not directly included within the DFT treatment and will be further discussed below.

The absorption spectrum of graphene is characterized by the well pronounced peak at approximately 4 eV corresponding to the transition at the saddle point (M point) in the Brillouin zone. The widely delocalized π electronic system in the perylene molecule gives rise to strong absorption peaks at 1.7, 3.6, and 4.9 eV. The obtained transition energies are lower than in experiment due to the shortcoming of the applied exchange-correlation functional. Calculations based on hybrid functionals give a much better agreement with the experiment. Since in this work we focus on the Förster and Dexter energy transfer mechanisms between the perylene molecule and graphene, the energetic deviations within PBE exchange-correlation function do not play a qualitative role. Due to the linear gapless band structure of graphene in the relevant energy region, there are always electronic states that are in resonance with the energetically lowest HOMO–LUMO transition of the perylene molecule.

Furthermore, we have investigated the charge rearrangement within the hybrid nanostructure. As already seen in Figure 2, the adsorbed molecule leads to a spatial pillow-like effect pushing the graphene’s carbon atoms further away and giving rise to a small dent of <0.1 Å. This also affects the mobility of charge carriers within the graphene layer resulting in charge rearrangements. Figure 5a shows a surface plot illustrating the molecule-induced charge density difference $\Delta \rho(x,y,z) = \rho_{\text{hybrid}} - \rho_{\text{graphene}} - \rho_{\text{perylene}}$ for the exemplary iso-value of $5 \times 10^{-5} \text{e} / \text{Å}^2$. One can clearly see the accumulation of negative (blue) and positive (red) charges. According to the pillow effect, the electrons are pushed away from the region directly below the molecule. As a result, this region is characterized by a positive charge, that is, the lack of electrons (red areas). At the same time, electrons accumulate further away at the graphene surface at the graphene-facing side of the molecule (blue areas). To further illustrate the charge distribution along the z-direction (perpendicular to the graphene surface), we show the plane-averaged charge density difference $\Delta \rho(z) = \int dx/\text{d}y \Delta \rho(z)$ and the charge difference $\Delta \rho(z) = \int z_0 \text{d}z' \Delta \rho(z')$, see Figure 5b and c, respectively. The charge distribution around the graphene layer qualitatively reflects the spatial shape of the most relevant $2p_z$ carbon orbitals reaching above and below the graphene sheet. A similar charge distribution can also be observed around the position of the perylene molecule, illustrating a positive (negative) charge accumulation slightly below (above) the molecule. Note, however, that the quantitative effect of charge rearrangements is relatively small. The predicted small charge difference of up to 0.02 $e_0$ is in agreement with what one would expect for a noncovalent functionalization.

The dashed lines in Figure 5 reflect the charge distribution obtained within constrained DFT calculations, that is, we imposed particular initial occupations of molecular HOMO and LUMO levels while solving the Kohn–Sham equations. The aim was to investigate the change of the substrate–molecule interaction once the molecule is optically excited. Therefore, we promoted one electron from the HOMO to the LUMO level.
The calculations show only marginal changes in the charge distribution (cf., Figure 5) or in the electronic band structure (not shown). This insight is important for the discussion of the excitation energy transfer in the investigated hybrid structure. To achieve this goal, we will combine the DFT-based knowledge of the hybrid material with the tight-binding-based analytic expression for the Förster transfer rate. Furthermore, we will discuss the Dexter transfer by exploiting our DFT study allowing us to estimate the overlap of the involved molecular and graphene orbitals.

The Förster and Dexter energy transfer rates can be analytically expressed via the Fermi golden rule

$$
\gamma = \frac{2\pi}{\hbar} \sum_{k} \sum_{l} W(\mathbf{v}_{k_{l}}, \mathbf{c}_{k_{l}}, l, h)^{2} \delta(\epsilon_{k_{l}} - \epsilon_{k_{l}} - \Delta E_{M})
$$

with the momentum-dependent initial and final states of the graphene substrate $\Phi_{M,k}^{\nu}(\mathbf{r})$ and the HOMO and LUMO states of the molecule $\Phi_{M}^{\nu}(\mathbf{r})$. The delta function makes sure that only energy-conserving processes contribute. The Förster rate $\gamma_{F}$ is determined by the direct contribution of the Coulomb interaction

$$
\gamma_{F} = \frac{2\pi}{\hbar} \sum_{k} \sum_{k'} d_{M} \sum_{\nu} |q_{\nu}^{\text{exc}}(k,k')|^{2} \frac{1}{\epsilon_{k_{l}} - \epsilon_{k_{l}} - \Delta E_{M}}
$$

For Dexter coupling, a large spatial overlap between graphene and molecular orbitals ($\Phi_{M,k}^{\nu}(\mathbf{r})\Phi_{M}^{\nu}(\mathbf{r})$) is of key importance.\cite{28,29} As a result, $\gamma_{D}$ shows an exponential dependence on the substrate-molecule distance $R$ and occurs only for small distances (typically, smaller than 10 Å).\cite{27,29,45} In contrast, the Förster coupling is dominated by the factor $1/(\epsilon_{k_{l}} - \epsilon_{k_{l}} - \Delta E_{M})$.

$$
\gamma_{D} = \frac{2\pi}{\hbar} \sum_{k} \sum_{k'} d_{M} \sum_{\nu} |q_{\nu}^{\text{exc}}(k,k')|^{2} \frac{1}{\epsilon_{k_{l}} - \epsilon_{k_{l}} - \Delta E_{M}}
$$

where $c_{0}$ denotes the elementary charge and $\epsilon_{0}$ the vacuum permittivity. The exchange Coulomb contribution gives the Dexter rate $\gamma_{D}$ with\cite{27,28,45}

$$
\gamma_{D} = \frac{2\pi}{\hbar} \sum_{k} \sum_{k'} d_{M} \sum_{\nu} |q_{\nu}^{\text{exc}}(k,k')|^{2} \frac{1}{\epsilon_{k_{l}} - \epsilon_{k_{l}} - \Delta E_{M}}
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Consider the conventional energy transfer between donor and acceptor molecules, the Förster coupling is based on the dipole–dipole interaction and is characterized by a $R^{-6}$ dependence.\cite{27,28,45} In the case of functionalized graphene, the substrate is not a spatially localized molecule, but a periodically extended two-dimensional nanostructure. Following the approach of Swathi et al.,\cite{40} the Förster coupling can be considered as an interaction of the molecular transition dipole $d_{M} = -c_{0} \int d\mathbf{r} \Phi_{M}^{\nu}(\mathbf{r})\Phi_{M}^{\nu}(\mathbf{r})$ located in the electrostatic potential $q_{\nu}^{\text{exc}}(\mathbf{r}) = (1/(4\pi\epsilon_{0})) \int d\mathbf{r} \rho_{\nu}^{\text{exc}}(\mathbf{r})/(\mathbf{r} - \mathbf{r'})$ arising from the transition charge density of graphene $\rho_{\nu}^{\text{exc}}(\mathbf{r})$. Then, the Förster energy transfer rate can be written as

$$
\gamma_{F} = \frac{2\pi}{\hbar} \sum_{k} \sum_{k'} d_{M} \sum_{\nu} |q_{\nu}^{\text{exc}}(k,k')|^{2} \frac{1}{\epsilon_{k_{l}} - \epsilon_{k_{l}} - \Delta E_{M}}
$$

where the electrostatic potential $q_{\nu}^{\text{exc}}(k,k')$ is evaluated at the fixed position of the molecule.

Combining DFT calculations on the molecular transition dipole moment with the tight-binding approximation of the graphene wave functions allows us to obtain an analytic expression for $\gamma_{F}$. For the molecular transition dipole moment, we obtain $d_{M} = (d_{d}d_{M}d_{f}) = (-0.80, 1.39, 4.92 \times 10^{-7}) c_{0} \text{ Å}$, with $d_{M} = 1.60 c_{0} \text{ Å}$. As expected for the flat perylene molecule lying in the $x$-$y$ plane, $d_{f}$ is nearly zero. The dipole moment is obtained for the perylene molecule that has been fully geometrically relaxed in the presence of the graphene substrate. Furthermore, we have also performed constrained DFT calculations\cite{43} modeling an initially excited molecule (one electron promoted from the HOMO into the LUMO level) to account for the changes of the molecular states due to the optical excitation taking place before the actual energy transfer process, as illustrated in Figure 1. Our calculations reveal only negligibly small changes of the dipole components in agreement with the marginal changes observed for the charge distribution in Figure 5.

Within the tight-binding approximation, the transition charge density of graphene $\rho_{\nu}^{\text{exc}}(\mathbf{r})$ can be obtained analytically. Taking
into account only the strongest overlaps one obtains for the Förster transfer rate

\[ \gamma_F(R) = \frac{\Delta E_M}{\sqrt{4 \pi \hbar^2 (d_1^2 + 2d_2^2)}} \frac{e^{-2qR}}{\Delta E_M - \nu_F \nu_D} \text{d}q \]

with the HOMO–LUMO gap \( \Delta E_M \) and the slope in the electronic band structure of graphene on. More details on the derivation of the Förster transfer rate can be found in the work of Swathi et al.\(^{30}\) Here, we focus on the evaluation of this expression for the investigated perylene-functionalized graphene. The Förster coupling explicitly depends on the square of the parallel \( d_1 \) (in the \( x-y \) plane) and the perpendicular component \( d_2 \) (z-axis) of the molecular transition dipole moment \( d_{\text{M}} \). Since we have already determined these characteristics for the perylene molecule within the graphene-based hybrid material, we can now explicitly evaluate the Förster energy transfer rate.

Figure 6 illustrates the Förster rate as a function of the substrate–molecule distance \( R \). Generally, the integral over all processes involving the momentum transfer \( q \) cannot be analytically solved. We find that, within the simplest tight-binding approximation taking into account only the strongest overlaps, the direct transitions with \( q = 0 \) do not contribute to the energy transfer. The inset of Figure 6 shows the integrand of eq 5 (denoted as \( \gamma_F R \)) as a function of \( q \) for different fixed distances \( R \). For \( R < 10 \) Å, \( \gamma_F R \) quickly increases with \( q \) and the Förster rate \( \gamma_F \) shows an exponential decay with \( R \), that is, \( \gamma_F \approx \alpha_1 e^{-qR} \) with \( \alpha_1 \approx 3.66 \text{ fs}^{-1} \) and \( \alpha_2 \approx 0.80 \text{ Å}^{-1} \), see Figure 6. For large distances, the behavior drastically changes: \( \gamma_F R \) is characterized by a maximum centered at \( q \approx 3/(2R) \), that is, only processes involving a certain momentum transfer \( q \) significantly contribute to the energy transfer rate. In the limit of large substrate–molecule distances (\( R \gg 10 \) Å), the Förster coupling exhibits a clear \( R^{-4} \) dependence, that is, \( \gamma_F \approx \alpha_1 R^{-4} \), with \( \alpha_1 \approx 42.85 \text{ fs}^{-1} \), see Figure 6. This is in excellent agreement with the observations in a recent experiment varying the distance between graphene and attached molecular emitters by depositing additional layers.\(^{26}\)

Inserting the molecular transition dipole moment \( d_{\text{M}} = (d_{\text{L}}, d_{\text{C}}) \) for the investigated exemplary perylene-functionalized graphene, we obtain a very efficient Förster energy transfer rate of \( \gamma_F(R) = 0.277 \text{ fs}^{-1} \). This can be traced back to the strong Coulomb interaction in the graphene substrate and the short substrate–molecule distance of \( R_0 = 3.25 \) Å obtained within a full geometric relaxation of the entire hybrid nanostructure. At such a short distance, transitions involving different momentum transfers \( q \) crucially contribute to the Förster rate, see the inset of Figure 6. Our result is in line with experimental time-resolved investigations of the energy transfer in functionalized carbon nanotubes, suggesting that the transfer process occurs on an ultrafast femtosecond time scale.\(^{46}\) Often, it is necessary to include additional linker molecules to experimentally achieve the functionalization\(^{22}\) resulting in much larger substrate–molecule distances. For example, \( R = 10 \) and \( 50 \) Å result in a Förster rate of \( \gamma_F = 4.88 \times 10^{-3} \text{ ps}^{-1} \) and \( 6.88 \times 10^{-3} \text{ ps}^{-1} \), respectively. The drastic decrease in efficiency is in agreement with the experimental findings of L. Gaudreau and co-workers.\(^{26}\)

In spite of the short distance between the graphene layer and the perylene molecule, our calculations reveal that the Dexter energy transfer rate \( \gamma_D \) is negligibly small compared to the discussed Förster transfer mechanism. The Dexter rate is determined by the spatial overlap between the strongly localized graphene and perylene orbitals. To estimate \( \gamma_D \), we calculate the ratio between the overlaps \( \alpha_D = \langle \Phi_{\text{L}}^*(r) \Phi_{\text{M}}(r) \rangle \) and \( \alpha_F = \langle \Phi_{\text{L}}^*(r) \Phi_{\text{L}}(r) \rangle \) appearing in the Dexter and the Förster rate, respectively, see eqns 2 and 3. We obtain \( \alpha_D/\alpha_F \approx 10^{-1} \). Since in the rates the square of the product of two such overlaps appears, the Dexter rate \( \gamma_D \) is expected to be approximately 4 orders of magnitude smaller than the Förster rate \( \gamma_F \).

\( \text{Figure 6. Förster energy transfer rate } \gamma_F \text{ as a function of the substrate–molecule distance } R. \text{ For short distances, the transfer rate is characterized by an exponential decay (orange line), while for large distances a } R^{-4} \text{ behavior (red line) is found. The inset shows the momentum dependence of the processes contributing to the Förster transfer rate at different constant substrate–molecule distances } R. \text{ Here, } \gamma_F R \text{ corresponds to the integrand of eq 5.} \)
In conclusion, we have investigated the energy transfer in perylene-functionalized graphene. Having characterized the hybrid material within DFT calculations including a fully geometric relaxation of the structure, its electronic band structure, optical properties, and charge rearrangements, we focus on the energy transfer that has been measured in recent experiments. Combining DFT-based calculation of the molecular transition dipole moment and tight-binding-based consideration of graphene wave functions allows us to obtain an analytic expression for the Förster energy transfer rate. Our calculations reveal strongly efficient Förster coupling with rates in the range of fs\(^{-1}\). In contrast, the Dexter energy transfer mechanism is found to be negligibly small due to small overlap between the involved strongly localized substrate and molecule orbital functions. The obtained results can be applied to other carbon-based hybrid nanostructures and in general to the description of energy transfer processes in molecular functionalized nanostructures, once the molecular dipole moment and the substrate–molecule separation are known.

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank the Einstein Foundation Berlin and the Deutsche Forschungsgemeinschaft (within the collaborative research center SFB 658) for financial support. O.T.H. acknowledges the support from FWF (Project: J 3285-N20). A.R. acknowledges financial support from the European Research Council (ERC-2010-AdG-267374), Spanish Grant (FIS2010-21282-C02-01), Grupos Consolidados UPV/EHU del Gobierno Vasco (IT578-13), and the EU Project (280879-2 CRONOS CP-FP7).

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