Dynamical tuning of energy transfer efficiency on a graphene monolayer

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In this contribution we present a theoretical investigation of the energy transfer efficiency between quantum systems placed in proximity of a monolayer of conducting graphene. We calculate the spontaneous emission rate of a quantum system and the energy transfer rate between a donor-acceptor pair, and thus the energy transfer efficiency, using a Green's tensor formalism. The direct interaction between the donor and acceptor dominates when they are close to each other, but is modified from its free-space behavior due to the presence of the graphene monolayer and its interaction with the donor and acceptor. We report on a very large influence of the graphene monolayer on the energy transfer efficiency due to both the Förster mechanism and the propagating graphene plasmon mode. In particular, the Förster radius R_0 is modified from its free-space value of 20 nm and can reach values of 120 nm when close to a graphene monolayer. As the donor-acceptor separation is increased, their direct interaction is overshadowed by the interaction via the surface plasmon mode. Due to the large propagation length of the surface plasmon mode on graphene, an energy transfer efficiency as high as 50% can still be achieved for distances as large as 300 nm. The interaction via the surface plasmon mode is tunable via the doping of the graphene monolayer and the surface plasmon channel can also be switched off this way.

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I. INTRODUCTION

For the last two decades the field of plasmonics has grown intensively. Confining light to subwavelength structures by exciting surface plasmon-polariton (SPP) modes has various applications in biosensing devices, light harvesting, optical nanoantennas, and quantum information processing. SPPs are collective oscillations of electrons and the electromagnetic field that are excited at the interface between a dielectric and a conductor and can propagate along that interface [1]. In plasmonics, noble metals are routinely used as the conducting medium. The main drawback of using noble metals in the applications mentioned above is their large ohmic losses [2].

Graphene constitutes an alternative to using noble metals for plasmonic applications [3–7]. It is a two-dimensional material possessing unique properties. This atomically thick monolayer has superior electronic and mechanical properties originating in part from its charge carriers of zero effective mass that can travel for microns without scattering at room temperatures [8].

An undoped graphene monolayer (GM) can absorb $\pi\alpha_0 \approx 2.3\%$ of the light incident upon it, where α_0 is the fine structure constant [9]. Patterned GM nanostructures can give rise to 100% absorption at specific wavelengths, which can be tuned through the applied voltage [10–12].

Interactions between quantum emitters (QEs) and a GM have been investigated intensively over the last few years, especially regarding the influence of the GM on the spontaneous emission (SE) rate of a QE placed near the GM [13–19]. It has been found that the SE rate can be enhanced by several orders of magnitude compared with its free space value, due to the excitation of graphene plasmon (GP) modes. Furthermore, confinement of the GP modes to one dimension (graphene ribbons) [12,17] and zero dimensions (graphene nanodisks) [11,17,20] can enhance the QE-GM interaction even more. In

the case of zero-dimensional confinement, the strong-coupling regime can be achieved between a QE and graphene nanodisks [17].

The presence of a second QE in the system will modify the emission properties of the system, giving rise to super- and subradiant states [21,22]. Furthermore, the confinement of the GP to one dimension (graphene ribbons) [23] or zero dimensions (graphene nanodisks) [20] further enhances the interaction rates. Although the SE of a QE in the presence of graphene nanostructures has been investigated thoroughly, the energy transfer (ET) rate between a pair of QEs in the presence of graphene nanostructures has garnered less attention. In particular, it is an open question whether or not it is possible to allow efficient interaction between a pair of QEs in the presence of a GM [24,25]. The authors of Ref. [24] have found an enhancement of the resonance ET rate of several orders of magnitude when compared to free-space, but have not investigated the energy transfer efficiency. In Ref. [25] the efficiency was considered and while it was significantly enhanced compared to free-space, the absolute values calculated were extremely small, thus discouraging any experimental investigation of the proposed structure. In our model, on the other hand, taking into account the SE rate modified by the presence of the GM [26], we can report energy transfer efficiencies above 50%, over distances of hundreds of nanometers along the GM, thus opening opportunities for experimental investigations of the coupled QE-graphene nanostructure.

In this contribution we calculate the SE and ET rates using a semianalytical Green's tensor formalism [27]. This approach has been applied to experimental results and good agreement was obtained [26]. We use quantum emitters with optical properties corresponding to real physical systems. The ET rate is calculated considering the influence of the SE on the QE-GM interaction. The SE and ET rates are competitive processes, thus an ET efficiency is introduced. The ET efficiency can be tuned, through gating of the GM, thus opening opportunities

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for applications such as switching and sensing devices [28–30], light harvesting [31], plasmonic rulers [29,32], and quantum computing [33]. Furthermore, we show that the ET rate along the GM has two contributions, a Förster contribution and a GP contribution, both of which can be tuned. At small donor-acceptor distances, the Förster contribution dominates and the Förster radius, the characteristic distance at which the ET efficiency is 50%, is enhanced significantly compared to the free-space value. Furthermore, as the separation is increased, the GP contribution begins to dominate, and the donor can efficiently transfer its excitation over hundreds of nanometers. We also show that the ET rate across the GM is mainly determined by the penetration depth of the GP mode.

The paper is structured as follows. We begin in Sec. II with a theoretical framework in which we introduce the optical properties of the GM and the GP mode it supports (Sec. II A), and we also identify the strong and weak coupling regimes of the QE-GM system (Sec. II B), since our Green's tensor approach holds only in the weak coupling regime. In Sec. III we present the results of our calculations for the SE rate (Sec. III A), the ET function (Sec. III B), and subsequently extract the ET efficiency (Sec. III C), for different distance regimes and values of the chemical potential. While the influence of the GM on the SE rate and the ET rate has been previously reported in the literature, it is essential to consider both in tandem to investigate the ET efficiency and therefore we include them here for completeness. Finally, in Sec. IV we give a summary of the results and the conclusions drawn. In addition, we include two Appendixes where we present various expressions used in the main body of the paper.

II. THEORETICAL FRAMEWORK

The model system considered in this paper is presented as a sketch in Fig. 1. We consider an atomically thin monolayer of graphene in the xy plane, suspended in vacuum. Close to this graphene monolayer, we have either a single quantum system, when investigating spontaneous emission, or two quantum systems, for energy transfer investigations. We begin our investigation by considering a conductivity model for graphene and the GP properties.

A. Graphene conductivity and GP properties

We calculate the graphene in-plane conductivity σ in the random phase approximation (RPA) [34–36]. This quantity is mainly controlled by electron-hole pair excitation that can

FIG. 1. (Color online) A graphene monolayer in the xy plane, with the quantum emitter approximated as a two level system.

FIG. 2. (Color online) GP dispersion relation in doped graphene $\hbar\omega(k_s)$ for different values of the chemical potential μ ; the dots show the quadratic approximation of the dispersion relation. The inset shows the propagation length of the GP mode L_{SP} for the same values of the chemical potential μ .

be divided into intraband and interband excitations. It can be written as

$$\sigma = \sigma_{\text{intra}} + \sigma_{\text{inter}}, \quad (1)$$

where the intraband and interband contributions are

$$\sigma_{\text{intra}} = \frac{2ie^2t}{\hbar\pi(\Omega + i\gamma)} \ln \left[2 \cosh \left(\frac{1}{2t} \right) \right], \quad (2)$$

$$\sigma_{\text{inter}} = \frac{e^2}{4\hbar} \left[\frac{1}{2} + \frac{1}{\pi} \arctan \left(\frac{\Omega - 2}{2t} \right) - \frac{i}{2\pi} \ln \frac{(\Omega + 2)^2}{(\Omega - 2)^2 + (2t)^2} \right]. \quad (3)$$

In the above we have introduced the dimensionless parameters $\Omega = \hbar\omega/\mu$, $\gamma = E_S/\mu$, and $t = k_B T/\mu$. Here μ is the chemical potential, T is the temperature, and E_S is the scattering energy. This scattering energy is related to the relaxation time τ through $\tau = \hbar/E_S$. The σ_{intra} term describes a Drude model response for intraband processes corrected with a term γ , which accounts for impurities compromising the electron's mobility. Throughout this paper we consider a temperature $T = 300$ K and a value of the relaxation time of $\tau = 1$ ps [37,38]. Figure 2 shows the dispersion relation $\omega(k_s)$ for different values of the chemical potential μ , where k_s is the in-plane wavevector. Due to the fact that retardation effects dominate for wave vectors $k_s > k_F$ and energies $\hbar\omega > 2\mu$, the GP dispersion curves in Fig. 2 terminate at these values, where k_F is the Fermi wave vector. When the chemical potential μ has the value $\mu = 0$, the GM absorbance has the value $\pi\alpha_0 \approx 2.3\%$, where α_0 is the fine structure constant. This is the asymptotic value of the doped GM for energies $\hbar\omega > 2\mu$. Considering that the GM is surrounded by air, $\epsilon_1 = \epsilon_2 = 1$ (free standing GM), the GP dispersion relation can be obtained from

$$\frac{1}{\sqrt{k_0^2 - k_{SP}^2}} = -\frac{2\pi\sigma}{\omega}, \quad (4)$$

where k_{SP} is the GP wave vector [17]. Because $k_{SP} \gg k_0$, we can simplify the dispersion relation above, using only the σ_{intra}

contribution, to obtain

$$k_{\text{SP}} = \frac{\hbar^2}{4e^2\mu k_B T \ln\left[2 \cosh\left(\frac{\mu}{k_B T}\right)\right]} \omega \left(\omega + \frac{i}{\tau}\right), \quad (5)$$

which has as its main feature the quadratic dependence of the GP wave vector on the frequency, when the intraband contributions dominate [34]. This approximate quadratic dependence is shown as dots in Fig. 2. Another feature of the GP dispersion relation on graphene is the fact that the GP resonance frequency is blueshifted as the chemical potential increases.

The inset in Fig. 2 shows the propagation length of the surface plasmon along the graphene $L_{\text{SP}} = 1/\text{Im}(k_{\text{SP}})$, as a function of energy, for different values of the chemical potential μ . It is evident from the plot that, depending on the value of the chemical potential μ , this propagation length can reach values as large as hundreds of microns at low frequencies. As the energy is increased, however, the propagation length decreases rapidly, because the GP then has sufficient energy to generate electron-hole pairs and the dispersion relation is dominated by the interband contributions [3].

B. Rabi splitting—strong coupling regime

In order to ascertain whether the weak or strong coupling regime applies for particular sets of parameters, we now consider a model consisting of a single QE interacting with the GP mode of the GM. To describe this system we use a Jaynes-Cummings Hamiltonian [39] of the form

$$H = \frac{\hbar\omega}{2}\sigma_z + \hbar\omega_{\text{SP}}\hat{a}^\dagger\hat{a} + \hbar g(\hat{a}\sigma_+ + \hat{a}^\dagger\sigma_-), \quad (6)$$

where ω_{SP} is the GP frequency, $\hat{a}^\dagger$ and $\hat{a}$ are the creation and annihilation operators of the plasmon mode, ω is the transition frequency of the QE between its ground and excited state, σ_+ and σ_- are the raising and lowering operators of the QE, and g is the coupling constant between the QE and the GP mode of the GM. The coupling constant g is given by [40]

$$\begin{aligned} |g(\omega)|^2 &= \frac{1}{\hbar\pi\epsilon_0} \frac{\omega^2}{c^2} \hat{\mathbf{d}}^T \text{Im}\mathfrak{G}_{\text{SP}}(\omega, \mathbf{r}_{\text{QE}}, \mathbf{r}_{\text{QE}}) \hat{\mathbf{d}} \\ &= \gamma_0 \frac{3c}{\omega} \hat{\mathbf{d}}^T \text{Im}\mathfrak{G}_{\text{SP}}(\omega, \mathbf{r}_{\text{QE}}, \mathbf{r}_{\text{QE}}) \hat{\mathbf{d}}, \end{aligned} \quad (7)$$

where $\mathfrak{G}_{\text{SP}}(\omega, \mathbf{r}_{\text{QE}}, \mathbf{r}_{\text{QE}})$ is the GP part of the Green's tensor, derived in Appendix A [Eq. (A2a)], γ_0 is the Einstein A coefficient, $\gamma_0 = \omega^3 d^2 / (3\pi \hbar \epsilon_0 c^3)$, and $\mathbf{d}$ is the transition dipole moment of the QE positioned at $\mathbf{r}_{\text{QE}} = (0, 0, z)$. In this section we consider $\gamma_0 = 5 \times 10^{-8} \text{ fs}^{-1}$ and we consider the transition dipole moment $\mathbf{d}$ of the QE to be oriented along z . Since we are interested in the coupling between the GP mode and the QE we calculate the GP contribution to Eq. (A2a) by extracting the pole contribution and we obtain

$$\mathfrak{G}_{S,zz}^{(1)\text{SP}}(z, \omega) = -\frac{1}{4} \frac{(1 - 1/\alpha^2)}{\alpha k_0} e^{-2iz/\alpha}, \quad (8)$$

where $\alpha = 2\pi\sigma/c$.

The Hamiltonian from Eq. (6) couples the states $|e\rangle \otimes |0\rangle$ and $|g\rangle \otimes |1\rangle$ to the dressed states $|1\rangle$ and $|2\rangle$ with energies

$$E_1 = \frac{\hbar\omega_{\text{SP}}}{2} - \frac{\hbar}{2}\sqrt{\delta^2 + 4g^2}, \quad (9a)$$

$$E_2 = \frac{\hbar\omega_{\text{SP}}}{2} + \frac{\hbar}{2}\sqrt{\delta^2 + 4g^2}, \quad (9b)$$

where $\delta = \omega_{\text{SP}} - \omega$ is the detuning between the GP mode resonant frequency and the transition frequency of the QE. The energy states are separated by $\Omega = \sqrt{\delta^2 + 4g^2}$, which gives the value of the Rabi splitting. As an example, if we consider the case where the QE is positioned at $z = 10 \text{ nm}$ above a GM with a chemical potential equal to the transition energy of the QE, $\mu = \hbar\omega = 0.5 \text{ eV}$, the Rabi splitting, at $\delta = 0$, has a value $2\hbar g(\omega) = 0.12 \text{ eV}$.

In order to further investigate the weak and strong coupling regimes, we will analyze the dependence of the coupling constant g on the various parameters involved, namely the value of the chemical potential μ , the emission frequency of the QE ω , and the distance of the QE to the GM z . Considering $\omega = \omega_{\text{SP}}$, i.e., zero detuning, the criterion for having strong coupling is whether or not the absorption spectrum of the system exhibits two peaks of different frequencies [40,41]. This condition is fulfilled if

$$|g| > \frac{1}{4} |\gamma_{\text{LSW}} - \kappa|, \quad (10)$$

where γ_{LSW} represents the *lossy surface waves* (LSW) contribution, which are nonpropagating evanescent modes relaxing through ohmic losses, and κ is the width of the $g(\omega)^2$ spectrum.

In Fig. 3(a) we present a contour plot of the quantity $\mathfrak{D} = 4|g|/|\gamma_{\text{LSW}} - \kappa|$ as a function of the chemical potential μ and the emission energy $\hbar\omega$ for a fixed position of the QE, $z = 10 \text{ nm}$. Although from condition (10) when $\mathfrak{D} < 1$ we are in the weak coupling regime, this condition might not be sufficient under some experimental conditions [39], and we thus consider the more stringent inequality $\mathfrak{D} \lesssim 0.5$ as giving the weak coupling condition. As is evident from Fig. 3(a), for chemical potential values $\mu < 0.3 \text{ eV}$ there exists a frequency region where we have $\mathfrak{D} \geq 0.5$ and the weak coupling approximation needed to calculate the SE and ET rates is no longer valid. This region where the strong coupling dominates corresponds to THz frequencies, a range outside the scope of our investigation. For chemical potential values $\mu > 0.6 \text{ eV}$, on the other hand, the quantity $\mathfrak{D}$ has values below 0.2, at all frequencies, well within the weak-coupling regime.

Figure 3(b) examines the maximum value of $\mathfrak{D}$ for different values of the chemical potential μ , and at different positions of the QE above the QM. For each point we calculate the maximum value of $\mathfrak{D}$ as a function of the emission energy of the QE, $\hbar\omega$. This represents, therefore, the worst-case scenario for weak coupling, since at all other frequencies, $\mathfrak{D}$ will be smaller than the values depicted in Fig. 3(b). It can be seen that the SC regime is only accessed for values of $\mu < 0.4 \text{ eV}$ at certain frequencies. Throughout the rest of the paper we only consider frequency ranges which remain outside the SC regime for all values of μ and g explored.

FIG. 3. (Color online) Contour plots of the quantity $\mathcal{D} = 4|g|/|\chi_{\text{LSW}} - \kappa|$ as a function of (a) chemical potential μ and emission energy $\hbar\omega$ normalized by the chemical potential for fixed QE position $z = 10$ nm, and (b) chemical potential μ and QE position z ; each point reflects the maximum value of $\mathcal{D}(\omega)$.

III. RESULTS AND DISCUSSION

A. Spontaneous emission rate

The decay rate γ is proportional to the strength of the coupling between the transition dipole matrix element and the electromagnetic modes acting on it. The normalized SE has the expression [27]

$$\tilde{\gamma} = \frac{\gamma}{\gamma_0} = n_i + \frac{6\pi c}{\omega} \text{Im}[\mathbf{n}_{\text{QE}} \cdot \mathfrak{G}_s(\mathbf{r}, \mathbf{r}, \omega) \cdot \mathbf{n}_{\text{QE}}], \quad (11)$$

where γ_0 is Einstein's A coefficient, $\mathbf{n}_{\text{QE}}$ is a unit vector along the direction of the transition dipole moment of the emitter, and $\mathfrak{G}(\mathbf{r}, \mathbf{r}, \omega)$ is given by (A2).

In Fig. 4(a) we have plotted the normalized SE rate $\tilde{\gamma}$ of a QE at a fixed position $\mathbf{r} = (0, 0, 10 \text{ nm})$ above the GM, as a function of the QE's emission energy $\hbar\omega$ for different values of the chemical potential μ . In general the SE rate has a peak at an energy below μ . As the energy is further increased, the SE rate drops dramatically before finally recovering to a value independent of μ , when the energy is above 2μ . As we increase the value of μ , the GP peak blueshifts and is broadened, and its value decreases. The general drop in the SE rate is most visible starting with values of the chemical potential of $\mu > 0.4$ eV,

and it occurs between the energies $\hbar\omega = \mu$ and $\hbar\omega = 2\mu$. This drop is due to interband transitions when the QE relaxes through lossy channels. At emission energies $\hbar\omega > 2\mu$ the emission is determined by interband contributions and GP excitations become unimportant, as the dispersion relations in Fig. 2 show. At these energies the SE rate follows the same behavior as for the case of undoped graphene $\mu = 0$ eV, as seen in Fig. 4(a). Moreover, we can see that the main contribution to the peak in the normalized SE rate $\tilde{\gamma}$ comes from the GP contribution, which is denoted by the circular symbols in Fig. 4(a). The maximum value of $\mathcal{D}$ is 0.41 at $\mu = 0.4$ eV, thus placing us within the weak coupling regime.

B. Energy transfer function

In this section we investigate the influence of the GM on the energy transfer process between a pair of QEs, a donor and an acceptor. The normalized energy transfer function which we investigate in this section is given as

$$\tilde{\Gamma} = \frac{\Gamma}{\Gamma_0} = \frac{|\mathbf{n}_A \cdot \mathfrak{G}(\mathbf{r}_A, \mathbf{r}_D, \omega) \cdot \mathbf{n}_D|^2}{|\mathbf{n}_A \cdot \mathfrak{G}_0(\mathbf{r}_A, \mathbf{r}_D, \omega) \cdot \mathbf{n}_D|^2} \quad (12)$$

[see also (B5)].

FIG. 4. (Color online) (a) SE rate of a QE, positioned at $\mathbf{r} = (0, 0, 10 \text{ nm})$, as a function of its emission frequency for different values of the chemical potential μ . (b) Normalized ET function $\tilde{\Gamma}(\mathbf{r}_A, \mathbf{r}_D, \omega)$ between a donor and acceptor QE as a function of frequency, for fixed donor and acceptor positions $\mathbf{r}_D = (0, 0, 10 \text{ nm})$ and $\mathbf{r}_A = (100, 0, 10 \text{ nm})$, respectively, and different values of the chemical potential μ .

FIG. 5. (Color online) Contour plots of the normalized ET function in the (a) xz plane and (b) xy plane when $z = 10$ nm, for a donor positioned at $\mathbf{r}_D = (0, 0, 10$ nm) above a GM. The dielectric permittivity of the surrounding media is $\epsilon_1 = \epsilon_2 = 1$. The chemical potential of the graphene monolayer is $\mu = 1.0$ eV. The emission frequency of the donor is $\omega = 0.8$ fs $^{-1}$ ($\lambda = 2.3$ μ m). Both donor and acceptor have their transition dipole moments oriented along the z axis.

Figure 4(b) shows the normalized energy transfer function $\tilde{\Gamma}$ as a function of frequency for different values of the chemical potential μ , and when both the donor and acceptor transition dipole moments are oriented perpendicular to the GM, i.e., zz orientation. The donor and acceptor positions are fixed at $\mathbf{r}_D = (0, 0, 10$ nm) and $\mathbf{r}_A = (100, 0, 10$ nm), respectively. As for the case of the SE rate in Fig. 4(a), the normalized ET function $\tilde{\Gamma}$ is enhanced close to the GP frequency and in general for frequencies $\hbar\omega < \mu$, where the intraband transitions dominate. For frequencies $\hbar\omega > \mu$ the energy transfer rate decreases due to the losses generated by the interband contributions.

Figure 5 presents contour plots of the normalized ET function $\tilde{\Gamma}$ as a function of the position of the acceptor in (a) the xz plane and (b) the xy plane 10 nm above the GM, when the donor position is fixed at $\mathbf{r}_D = (0, 0, 10$ nm), the transition energy is $\hbar\omega = 0.52$ eV ($\lambda = 2.3$ μ m), and the chemical potential is $\mu = 1.0$ eV. In Fig. 5(a) the normalized

ET function has large values when the acceptor is close to the GM and decreases as the acceptor distance is increased. This behavior is due to the fact that the field is highly confined in the z direction at the surface of the GM, with a penetration depth of $\delta_{SP} = 10$ nm, or $\delta_{SP}/\lambda = 4 \times 10^{-3}$. The fringes visible in Fig. 5(a) are due to the constructive and destructive interference between the direct and scattering terms in the Green's tensor, cf. Eq. (A1). This effect is more profound due to the dipole moment orientations of the QEs, along the z axis. Figure 5(b) shows that the normalized ET function has cylindrical symmetry in the xy plane, due to the orientation of both donor and acceptor transition dipole moments along the z axis. Furthermore, we see that the normalized ET function has a peak value at a distance of about 400 nm, which is the propagation length of the GP mode for the particular set of parameters used in this calculation.

In Fig. 6(a) we present the z dependence of the normalized ET function $\tilde{\Gamma}$ for a donor located at $\mathbf{r}_D = (0, 0, z)$ and an

FIG. 6. (Color online) Normalized ET function $\tilde{\Gamma}(\mathbf{r}, \mathbf{s}, \omega)$ as a function of the donor and acceptor distance to the graphene monolayer, for a fixed transition energy $\hbar\omega = 0.33$ eV. (a) For various values of the chemical potential μ when the donor position is $\mathbf{r}_D = (0, 0, z)$ and the acceptor position is $\mathbf{r}_A = (100$ nm, $0, z)$. (b) For various in-plane distances x when the donor position is $\mathbf{r}_D = (0, 0, z)$ and the acceptor position is $\mathbf{r}_A = (x, 0, z)$, for a fixed value of the chemical potential $\mu = 0.4$ eV. The symbols represent the full simulation data, while the lines are fits with the exponential function in the legend. Both donor and acceptor have their transition dipole moments oriented along the z axis.

TABLE I. GP penetration depths.

$\hbar\omega$ (eV)	μ (eV)	δ_{SP} (nm)	B_{SE} (nm)	B_{ET} (nm)
0.33	0.4	8.2	8.50	8.68
0.33	0.6	14.06	14.38	14.72
0.33	0.8	19.48	20.04	20.10
0.33	1.0	24.76	25.47	25.96

acceptor at $\mathbf{r}_A = (100 \text{ nm}, 0, z)$, for various values of the chemical potential, and a fixed transition energy $\hbar\omega = 0.33 \text{ eV}$. As we have already pointed out, for different values of the chemical potential μ , the position of the maximum in the normalized ET function blueshifts as the value of the chemical potential is increased, cf. Fig. 4(b). Thus, for the smallest value of the chemical potential $\mu = 0.2 \text{ eV}$, the enhancement of the ET function is negligible to nonexistent. As the value of the chemical potential is increased, the ET function has values a few orders of magnitude larger than in free-space when the donor-acceptor pair is close to the GM. As the donor-acceptor pair is moved further from the GM—increasing z —the ET function drops off exponentially, as the figure shows. The continuous lines in Fig. 6(a) represent fits of the calculated ET function (represented by symbols) with the exponential function $Ae^{-4z/B}$. The factor 4 in this expression has two sources: (i) the z distance of both donor and acceptor to the GM is varied and (ii) the ET function depends on the square of the field, see Eq. (12); each of these gives a doubling of the exponent, for a total of $2 \times 2 = 4$. Furthermore, because the donor-acceptor separation is kept constant at $x = 100 \text{ nm}$, the free-space ET function is also constant and, hence, does not influence the exponential behavior. Table I shows the values of the parameter B_{ET} extracted from the fit, together with the analogous parameter B_{SE} extracted from fitting the SE dependence (the numerical factor in the exponent is 2 in this case, rather than 4, due to the fact that the SE rate depends linearly on the electric field; data not shown) and the penetration depth of the GP in the air above the graphene, calculated as $\delta_{\text{SP}} = 1/\text{Im}(k_z^{\text{SP}})$. As this table shows, the values of the parameters B_{SE} and B_{ET} match closely the calculated penetration depths of the GPs. This suggests that the main channel for enhancing the ET function between the QEs is the GP resonance. As the separation between the two QEs becomes smaller and smaller, this relaxation channel becomes less and less important and the direct interaction dominates at distances below $x = 20 \text{ nm}$, as Fig. 6(b) shows. In Fig. 6(b) we consider the influence of the in-plane distance between the donor and acceptor, for a fixed value of the chemical potential $\mu = 0.4 \text{ eV}$ and fixed transition energy $\hbar\omega = 0.33 \text{ eV}$. We again fit the calculated ET function data (symbols) with the expression $Ae^{-4z/B}$. As one can see, above $x = 50 \text{ nm}$ the B_{ET} parameter extracted is very close to the penetration depth of the GP, δ_{SP} . When the donor and acceptor in-plane distance is smaller than $x = 50 \text{ nm}$, the influence of the GP mode on the ET function is less profound, and, as the donor-acceptor pair is moved away from the GM, it recovers its free-space interaction at shorter distances. This is due to the fact that the influence of the homogeneous part of the Green's tensor dominates over the scattered part, cf. Eq. (A1); this effect will

be further discussed in Sec. III C. In this section the quantity $\mathfrak{D}$ has the largest value of 0.48 for $\mu = 0.4 \text{ eV}$, $\hbar\omega = 0.33 \text{ eV}$ at a donor-GM distance of 8 nm, confirming that the system is in the weak coupling regime.

C. Energy transfer efficiency

In the previous section we investigated the SE and ET functions. When the donor dipole is excited it has two ways of relaxing to the ground state: it can either transfer its excitation energy to the acceptor dipole with an ET rate k_{ET} , or it can relax with decay rate k_{SE} , where it is assumed that there is no nonradiative decay, i.e., the intrinsic quantum yield of the donor is $Y_0 = 1$. The decay rate k_{SE} takes account of photon emission into the far field, coupling to GP modes, and losses in the GM. The SE and ET processes are, therefore, in competition with each other and we introduce an energy transfer efficiency to describe this competition.

We define the energy transfer efficiency η as

$$\eta = \frac{k_{\text{ET}}}{k_{\text{SE}} + k_{\text{ET}}}. \quad (13)$$

This quantity gives the relative contribution of the energy transfer process to the total decay rate of the donor. If the ET efficiency η has a value $\eta > 50\%$, then the decay of the excited state of the donor occurs mainly by energy transfer to the acceptor, rather than relaxation into photon or GP modes.

We next consider a donor-acceptor pair. The donor emission and acceptor absorption spectra are both given by a Gaussian distribution

$$A_q e^{-(\lambda - \lambda_q)^2 / \Delta\lambda_q^2}, \quad (14)$$

where $q = \text{D}$ represents the donor and $q = \text{A}$ represents the acceptor. A_q is a normalization constant, λ_q gives the position of the spectral peak, and $\Delta\lambda_q$ is related to the full width at half maximum (FWHM) of the spectrum. The donor emission peak and acceptor absorption maximum coincide at $\lambda_{\text{D}} = \lambda_{\text{A}} = 2 \mu\text{m}$. There are a variety of emitters at this wavelength, such as quantum dots and synthesized molecules [42,43]. The normalization constant of the donor emission spectrum $f_{\text{D}}(\lambda)$ is given as $A_{\text{D}}^{-1} = \int_0^\infty d\lambda f_{\text{D}}(\lambda)$. The width of the spectrum will be $\Delta\lambda_{\text{D}} = 20 \text{ nm}$, a reasonable value for a typical QE. The normalization constant for the acceptor absorption spectrum is $A_{\text{A}} = 0.021 \text{ nm}^2$, while the width is $\Delta\lambda_{\text{A}} = 50 \text{ nm}$.

The Förster radius R_0 is defined as the donor-acceptor separation at which the energy transfer efficiency η is 50%. R_0 is calculated from the spectral overlap of the normalized donor emission f_{D} and acceptor absorption σ_{A} spectra as

$$R_0 = \left[\frac{3c}{32\pi^4 n_r^4} \int_0^\infty d\lambda \lambda^2 f_{\text{D}}(\lambda) \sigma_{\text{A}}(\lambda) \right]^{1/6}, \quad (15)$$

where n_r is the refractive index of the host medium, in our case air with $n_r = 1$. For our case the Förster radius, R_0 , has a value of 19 nm in free space.

In Fig. 7 we present contour plots of the ET efficiency for the donor-acceptor pair, with spectral properties described above; the donor and acceptor positions are fixed at $\mathbf{r}_{\text{D}} = (0, 0, 10 \text{ nm})$, and $\mathbf{r}_{\text{A}} = (x, 0, z)$, respectively. The chemical potential takes on two values, Fig. 7(a) $\mu = 1.0 \text{ eV}$ and Fig. 7(b) $\mu = 0.6 \text{ eV}$.

FIG. 7. (Color online) Contour plot of the ET efficiency η between a pair of QEs, as a function of acceptor position for a fixed position of the donor at $\mathbf{r}_D = (0, 0, 10 \text{ nm})$ and different values of the chemical potential, (a) $\mu = 1 \text{ eV}$ and (b) $\mu = 0.6 \text{ eV}$. The green line gives the $\eta = 50\%$ values.

When $\mu = 1.0 \text{ eV}$ the emission and absorption spectrum overlap strongly with the ET function. For this case the ET efficiency η has values above 70% even for separations along the GM as large as 100 nm, and the 50% efficiency distance is around 300 nm. This value is very large compared to the free-space Förster radius of $R_0 = 19 \text{ nm}$. When the value of the chemical potential is $\mu = 0.6 \text{ eV}$, the ET efficiency η has values above 50% for separations above 100 nm but now the overlap between the emission and absorption spectra and the ET function is poorer, thus showing a diminished effect. The large confinement of light at the atomically thin GM surface can be used to efficiently transfer energy between a pair of QEs over large separations. Furthermore, this ET efficiency η can be controlled through gating of the GM, thus opening striking opportunities for possible applications, such as switching and sensing devices [28–30], light harvesting [31], plasmonic rulers [29,32], and quantum computing [33].

We next consider the behavior of the ET rate k_{ET} as a function of the in-plane separation between donor and acceptor. Figures 8(a) and 8(b) show the ET rate k_{ET} as a function of the in-plane separation between the donor and acceptor, when their elevation above the GM is (a) $z_D = z_A = 5 \text{ nm}$ and (b) $z_D = z_A = 10 \text{ nm}$ on the same side of the GM. For both panels we have fitted the near field with a Förster-type model $(R_0/x)^n$, where R_0 is the Förster radius. At small separations the fit yields the values $n = 6$ typical of Förster ET, but we see that the Förster radius is modified from the free-space value. At small separations $x < 10 \text{ nm}$, for $z_D = z_A = 5 \text{ nm}$ and $x < 20 \text{ nm}$, for $z_D = z_A = 10 \text{ nm}$, the ET rate k_{ET} follows an $n = 6$ dependence showing that the homogeneous part of the Green's tensor dominates, cf. (A1a), modified by the donor-acceptor interaction with the GM. Thus, there is an enhancement of the Förster radius, which depends on the donor-acceptor distances from the GM and the value of the chemical potential μ . In Fig. 8(a) the Förster radius has a value of $R_0 = 123.0 \text{ nm}$ for chemical potential values $\mu = 0.8 \text{ eV}$ and $\mu = 1.0 \text{ eV}$. As the chemical potential value drops, the Förster radius decreases to $R_0 = 91.0 \text{ nm}$ for $\mu = 0.4 \text{ eV}$, a value that is smaller than the one for the case of an undoped graphene layer $R_0 \approx 100 \text{ nm}$, due to the interband transitions, cf. Fig. 4(a). The effect of tuning the Förster radius through the chemical potential is evident.

In Fig. 8(b) the values of the Förster radius are smaller for the different values of the chemical potential μ due to the fact the QEs-GM distance is increased. When $\mu = 1.0 \text{ eV}$ we have the largest value of the Förster radius $R_0 = 94.3 \text{ nm}$ due to our choice of the donor and acceptor. For the off-resonance case $\mu = 0.4 \text{ eV}$, the Förster radius is $R_0 \approx 54.2 \text{ nm}$, once again smaller than the case of undoped graphene $R_0 \approx 70 \text{ nm}$.

At larger donor-acceptor separations we use the following expression to fit the calculated ET rate:

$$f(x) = \frac{A}{x} \exp\left(-\frac{2x}{B}\right), \quad (16)$$

which represents the dependence of the GP field intensity on the in-plane separation x (the factor 2 in the exponential results from the square of the Green's tensor, as does the x in the denominator—the GP field has a factor of $1/\sqrt{x}$). The fitting parameter B is tabulated in Table II, together with the corresponding propagation length of the GP along the interface of the GM, L_{SP} . As is clear, the correspondence between these parameters is very good indeed, confirming that, away from the near field, the interaction between donor and acceptor occurs primarily through the GP excited by the donor at the surface of the GM. As we increase the distance between the QEs and the GM, the Förster regime dominates further away from the near field, as can be seen from the fact that the intersection between the two fitting curves moves to larger distances. This is due to the small value of the penetration depth of the GP, $\delta_{\text{SP}} = 6.6 \text{ nm}$ at $\mu = 1.0 \text{ eV}$. In the next paragraph we will further consider the influence of the penetration depth to the ET rate k_{ET} .

Figures 8(c) and 8(d) consider the ET rate k_{ET} as a function of the donor-acceptor separation, for the case when the donor

TABLE II. GP propagation length.

$z \text{ (nm)}$	$\mu \text{ (eV)}$	$L_{\text{SP}} \text{ (nm)}$	$B \text{ (nm)}$
5	0.8	379.23	376.82
5	1.0	890.31	884.86
10	0.8	379.23	376.99
10	1.0	890.31	886.47

FIG. 8. (Color online) (a) and (b) ET rate k_{ET} as a function of the donor-acceptor in-plane separation x for fixed donor positions (a) $\mathbf{r}_D = (0,0,5 \text{ nm})$ and (b) $\mathbf{r}_D = (0,0,10 \text{ nm})$, respectively, and variable acceptor position $\mathbf{r}_A = (x,0,5 \text{ nm})$ and $\mathbf{r}_A = (x,0,10 \text{ nm})$, respectively, for different values of the chemical potential μ . (c) and (d) ET rate k_{ET} as a function of the donor-acceptor separation d for fixed donor positions (c) $\mathbf{r}_D = (0,0,5 \text{ nm})$ and (d) $\mathbf{r}_D = (0,0,10 \text{ nm})$, respectively, and variable acceptor position $\mathbf{r}_A = (0,0,z_A)$, with $d = z_D - z_A$ and for different values of the chemical potential μ .

position is kept fixed at Fig. 8(c) $z_D = 5 \text{ nm}$ and Fig. 8(d) $z_D = 10 \text{ nm}$ above the GM, and the separation between the donor-acceptor $d = z_D - z_A$ is varied, for $\mu = 1.0 \text{ eV}$ and $\mu = 0.4 \text{ eV}$. At small separations we again use the Förster model fitting presented earlier. To fit the behavior of the ET rate k_{ET} below the GM we choose the expression $f(z) = Ae^{-2z/B}$, where the parameter B will be connected with the penetration depth of the GP, δ_{SP} . In both figures the GM position is denoted by the dashed vertical line. In Fig. 8(c), for which the donor position is very close to the GM ($z_D = 5 \text{ nm}$), the behavior of the ET rate immediately below the GM is not trivial and comes from various contributions, such as direct interaction and GP coupling. On the other hand, in Fig. 8(d), for which $z_D = 10 \text{ nm}$, we can use the fitting function $f(z_A)$, and find for B the value $B = \delta_{SP} = 6.6 \text{ nm}$, showing that the main contribution to the ET rate comes from the GP on the GM. For the $\mu = 0.4 \text{ eV}$ case the ET rate k_{ET} is almost uninfluenced by the presence of the GM. The quantity $\mathcal{D}$ has a

maximum value of 0.2 for the donor-GM distance of 5 nm and $\mu = 1.0 \text{ eV}$.

IV. SUMMARY AND CONCLUSIONS

We have considered in this contribution the behavior of quantum systems placed near a free-standing graphene monolayer. The graphene monolayer can support graphene surface plasmon modes, tightly confined to the surface and having large propagation distances along the graphene monolayer.

We have begun by investigating the conditions of strong and weak coupling between a quantum system and the surface plasmon-polariton on the graphene monolayer. We have seen that for reasonably large values of the chemical potential $\mu > 0.4 \text{ eV}$ and any transition energies of the QE not in the THz regime, the weak coupling conditions are fulfilled. We can thus calculate such quantities as spontaneous emission

and energy transfer functions. We have found that both of these quantities are enhanced, compared to their free space values, due to efficient coupling to the graphene plasmon modes.

Due to the competition of the donor-acceptor energy transfer process with other donor decay processes, we have defined the energy transfer efficiency η and have investigated the influence of the graphene plasmons on this quantity. We have shown that the energy transfer efficiency η can reach values above 50% for distances up to 300 nm along the graphene monolayer. This process can be controlled by tuning the value of the chemical potential, e.g., through gating.

Finally, we investigate the ET rate k_{ET} varying the donor-acceptor in-plane separation and distance from the GM, for various values of the chemical potential μ . The ET rate, when the in-plane distance between the donor and acceptor is varied, has two major contributions: the Förster-type mechanism dominates at small separations, while the GP contribution dominates at large distances. The Förster-type ET rate follows a x^{-6} dependence, with an increased Förster radius value, due to the presence of the GM. The Förster radius value is increased from a value of $R_0 = 91.0$ nm when $\mu = 0.4$ eV, to $R_0 = 123.0$ nm when $z_D = z_A = 5$ nm and $\mu = 1.0$ eV. At larger distances, the main contribution comes from the GP propagation; the transition from the Förster to the GP-propagation mechanism depends on the distance of the donor-acceptor pair from the GM, and it occurs at donor-acceptor separations ranging from a few nanometers to a couple of tens of nanometers. When the z distance between donor-acceptor is varied, for $x = 0$, the behavior is somewhat more complicated, but the GP penetration depth still dictates the interaction length. As the chemical potential μ decreases the ET rate approaches the value for the case of undoped graphene. Thus, by varying the value of the chemical potential, we can tune the interaction channel or preferentially couple different species of resonant donor-acceptor pairs of QEs.

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APPENDIX A: GREEN'S TENSOR FORMALISM

We will consider two planar half-spaces with different dielectric permittivities ϵ_1 and ϵ_2 . The z direction is perpendicular to the boundary between the two half-spaces. In order to calculate the Green's tensor for this system, we use the method of scattering superposition [44]. The Green's tensor has the form

$$\mathfrak{G}^{(11)}(\mathbf{r}, \mathbf{s}, \omega) = \mathfrak{G}_h^{(11)}(\mathbf{r}, \mathbf{s}, \omega) + \mathfrak{G}_s^{(11)}(\mathbf{r}, \mathbf{s}, \omega), \quad (\text{A1a})$$

$$\mathfrak{G}^{(21)}(\mathbf{r}, \mathbf{s}, \omega) = \mathfrak{G}_s^{(21)}(\mathbf{r}, \mathbf{s}, \omega), \quad (\text{A1b})$$

where the first of the two labels in the superscript ($i1$) denotes the field point, while the second denotes the source point. The subscript s denotes the scattering term, always present, while the homogeneous term $\mathfrak{G}_h^{(11)}(\mathbf{r}, \mathbf{s}, \omega)$ contributes only when the source and field points are in the same medium.

The scattering terms have the following expression:

$$\begin{aligned} \mathfrak{G}_s^{(11)}(\mathbf{r}, \mathbf{s}, \omega) = & \frac{i}{8\pi^2} \sum_K \int d^2k_\rho \frac{1}{k_{z1}k_\rho^2} R_K^{+11-} \mathbf{K}(k_\rho, k_{z1}, \mathbf{r}) \\ & \otimes \mathbf{K}^*(k_\rho, -k_{z1}, \mathbf{s}), \end{aligned} \quad (\text{A2a})$$

$$\begin{aligned} \mathfrak{G}_s^{(21)}(\mathbf{r}, \mathbf{s}, \omega) = & \frac{i}{8\pi^2} \sum_K \int d^2k_\rho \frac{1}{k_{z1}k_\rho^2} R_K^{-11-} \mathbf{K}(k_\rho, -k_{z2}, \mathbf{r}) \\ & \otimes \mathbf{K}^*(k_\rho, -k_{z1}, \mathbf{s}), \end{aligned} \quad (\text{A2b})$$

where $k_\rho = \sqrt{k_i^2 - k_{zi}^2}$ is the in-plane propagation constant, k_{zi} is the perpendicular propagation constant in medium i , and $k_i = \frac{\omega}{c} \sqrt{\epsilon_i}$ is the wave number in medium i ($i = 1, 2$). The above expressions involve a summation over $\mathbf{K}$ which represents $\mathbf{M}$ and $\mathbf{N}$, or the transverse electric (TE) and transverse magnetic (TM) modes.

We impose the following continuity conditions at the boundary between the two half-spaces, $z = 0$:

$$\hat{z} \times [\mathfrak{G}^{(11)}(\mathbf{r}, \mathbf{s}, \omega) - \mathfrak{G}^{(21)}(\mathbf{r}, \mathbf{s}, \omega)]_{z=0} = 0, \quad (\text{A3a})$$

$$\begin{aligned} \hat{z} \times [\nabla \times \mathfrak{G}^{(11)}(\mathbf{r}, \mathbf{s}, \omega) - \nabla \times \mathfrak{G}^{(21)}(\mathbf{r}, \mathbf{s}, \omega)]_{z=0} \\ = -i \frac{4\pi}{c} k_0 \sigma \hat{z} \times \hat{z} \times \mathfrak{G}^{(21)}(\mathbf{r}, \mathbf{s}, \omega), \end{aligned} \quad (\text{A3b})$$

where σ is the surface conductivity.

Using Eqs. (A2) in (A3) we obtain the generalized Fresnel coefficients, which have the form [13,45]

$$R_M^{11} = \frac{k_{z1} - k_{z2} - 2\alpha k_0}{k_{z1} + k_{z2} + 2\alpha k_0}, \quad (\text{A4a})$$

$$R_N^{11} = \frac{k_2^2 k_{z1} - k_1^2 k_{z2} + 2\alpha k_0 k_{z1} k_{z2}}{k_2^2 k_{z1} + k_1^2 k_{z2} + 2\alpha k_0 k_{z1} k_{z2}},$$

$$R_M^{21} = \frac{2k_{z1}}{k_{z1} + k_{z2} + 2\alpha k_0}, \quad (\text{A4b})$$

$$R_N^{21} = \frac{2k_1 k_2 k_{z1}}{k_2^2 k_{z1} + k_1^2 k_{z2} + 2\alpha k_0 k_{z1} k_{z2}},$$

where $\alpha = 2\pi\sigma/c$.

APPENDIX B: SPONTANEOUS EMISSION AND ENERGY TRANSFER RATES

The spontaneous emission function γ has the form [46,47]

$$\gamma(\mathbf{r}, \omega) = \frac{2\omega^2 \mu^2}{\hbar \epsilon_0 c^2} \text{Im}[\mathbf{n}_\mu \cdot \mathfrak{G}(\mathbf{r}, \mathbf{r}, \omega) \cdot \mathbf{n}_\mu], \quad (\text{B1})$$

where $\mathbf{n}_\mu$ is a unit vector along the direction of the transition dipole moment of the emitter μ and $\mathfrak{G}(\mathbf{r}, \mathbf{r}, \omega)$ is the Green's tensor introduced in Appendix A.

A useful quantity to introduce is the normalized SE rate, defined as

$$\tilde{\gamma} = \frac{\gamma}{\gamma_0} = n_i + \frac{6\pi c}{\omega} \text{Im}[\mathbf{n}_\mu \cdot \mathfrak{G}_s(\mathbf{r}, \mathbf{r}, \omega) \cdot \mathbf{n}_\mu], \quad (\text{B2})$$

where the expression for γ_0 is given by the Einstein A coefficient as $\gamma_0 = \omega^3 \mu^2 / (3\pi \hbar \epsilon_0 c^3)$. The subscript s on the Green's tensor denotes the scattering part of this quantity,

which we introduced in Eqs. (A1) and $n_i = \sqrt{\epsilon_i}$ is the refractive index of the medium into which the quantum system is embedded. The normalized SE rate gives either an enhancement ($\tilde{\gamma} > 1$) or a reduction ($\tilde{\gamma} < 1$) of the SE rate compared to its free-space value γ_0 .

When dealing with statistical ensembles of emitters, the emission spectrum will be different from that of a single emitter, which we have taken to have a δ shape. The emission rate for the ensemble can then be expressed as

$$k_{SE} = \int_0^\infty d\lambda f_D(\lambda) \gamma(\lambda), \quad (B3)$$

where $f_D(\lambda)$ is the area-normalized emission spectrum of the emitter, with $\int_0^\infty d\lambda f_D(\lambda) = 1$.

Furthermore, we introduce the ET function Γ between a donor-acceptor pair, which has the form [27]

$$\Gamma(\mathbf{r}_A, \mathbf{r}_D, \omega) = \frac{2\pi}{\hbar^2} \left(\frac{\omega^2}{c^2 \epsilon_0} \right)^2 |\boldsymbol{\mu}_A \cdot \mathfrak{G}(\mathbf{r}_A, \mathbf{r}_D, \omega) \cdot \boldsymbol{\mu}_D|^2, \quad (B4)$$

where again $\mathfrak{G}(\mathbf{r}_A, \mathbf{r}_D, \omega)$ is the Green's tensor for the particular geometry, $\mathbf{r}_{D(A)}$ is the position of the donor D (acceptor A), and $\boldsymbol{\mu}_{D(A)}$ is the transition dipole moment of the donor D (acceptor A). The above expression for the energy transfer function depends on the donor-acceptor pair through the emission frequency of the donor and the transition dipole moment of the donor and acceptor. The influence of the

geometry is completely encapsulated in the Green's tensor, being proportional to the electric field intensity, through the square of the Green's tensor.

To consider only the influence of the geometry on a general donor-acceptor pair, we now introduce the normalized ET function for the system $\tilde{\Gamma}$ defined as

$$\tilde{\Gamma}(\omega) = \frac{\Gamma(\omega)}{\Gamma_0(\omega)} = \frac{|\mathbf{n}_A \cdot \mathfrak{G}(\mathbf{r}_A, \mathbf{r}_D, \omega) \cdot \mathbf{n}_D|^2}{|\mathbf{n}_A \cdot \mathfrak{G}_0(\mathbf{r}_A, \mathbf{r}_D, \omega) \cdot \mathbf{n}_D|^2}, \quad (B5)$$

where $\mathfrak{G}_0(\mathbf{r}_A, \mathbf{r}_D, \omega)$ is the Green's tensor in free space and $\mathbf{n}_{D(A)}$ is a unit vector in the direction of $\boldsymbol{\mu}_{D(A)}$.

Analogously to the case of the SE rate, when considering statistical ensembles of donors and acceptors, the donor emission spectrum $f_D(\lambda)$ and acceptor absorption cross-section $\sigma_A(\lambda)$ need to be taken into account when calculating the energy transfer rate. We therefore have [26]

$$k_{ET} = 36\pi^2 Y_D k_{SE} \int_0^\infty \frac{d\lambda}{\lambda^2} f_D(\lambda) |\mathbf{n}_A \cdot \mathfrak{G}(\mathbf{r}_A, \mathbf{r}_D, \lambda) \cdot \mathbf{n}_D|^2 \sigma_A(\lambda), \quad (B6)$$

where Y_D is the intrinsic quantum yield of the donor. We have used this expression to calculate the energy transfer rate between donors and acceptors with specific emission and absorption spectra and to investigate how the energy transfer process competes with the emission process of the donor.

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