Chapter 3
Nonradiative Energy Transfer in Assembly of Nanostructures

This chapter is reprinted (adapted) with permission from Ref. [1]. Copyright 2014 American Chemical Society. Here, we present the theoretical framework of generalized Förster-type nonradiative energy transfer (FRET) between one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) assemblies of nanostructures consisting of mixed dimensions in confinement, namely, nanoparticles (NPs) and nanowires (NWs). Also, the modification of FRET mechanism with respect to the nanostructure serving as the donor versus the acceptor is discussed, focusing on the rate's distance dependency. Here, the combinations of X → 1D assembly of NPs, X → 2D assembly of NPs, X → 3D assembly of NPs, X → 1D assembly of NWs, and X → 2D assembly of NWs (where X is an NP, an NW, or a quantum well (QW) with the donor → acceptor (D → A) denoting the energy transfer directed from the donor to the acceptor) are specifically considered because they are important for practical applications. Furthermore, here we give a complete set of analytical expressions in the long distance approximation, for FRET in all of the cases mentioned above and derive generic expressions for the dimensionality involved to present a complete picture and unified understanding of FRET for nanostructure assemblies.

Let us first consider the energy transfer process from a single nanostructure (NP, NW, or QW) to assemblies of NPs and NWs. Specifically, we look at the following cases: (1) NP → 1D NP assembly (linear chain); (2) NP → 2D NP assembly (NPs layer or plane); (3) NP → 3D NP assembly; (4) NP → 1D NW assembly (plane); (5) NP → 2D NW assembly; (6) NW → 1D NP assembly; (7) NW → 2D NP assembly; (8) NW → 3D NP assembly; (9) NW → 1D NW assembly; (10) NW → 2D NW assembly; (11) QW → 1D NP assembly; (12) QW → 2D NP assembly; (13) QW → 3D NP assembly; (14) QW → 1D NW assembly; and (15) QW → 2D NW assembly. For all cases, an analytical expression for the

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long distance approximation is given. We start this section with the macroscopic approach to the problem of dipole-dipole energy transfer.

The probability of an exciton transfer from the excited state of the donor nanostructure (donor) to the ground state of the acceptor nanostructure (acceptor) is given by the Fermi's Golden rule (3.1)

$$\gamma_{trans} = \frac{2}{\hbar}\left\{\sum_{f}\left|\langle f_{exc};0_{exc}|\hat{V}_{\text{int}}|i_{exc};0_{exc}\rangle\right|^{2}\delta\left(\hbar\omega_{exc}-\hbar\omega_{f}\right)\right\} \tag{3.1}$$

where $|i_{exc};0_{exc}\rangle$ is the initial state with an exciton in the donor and zero exciton in the acceptor; $|f_{exc};0_{exc}\rangle$ is the final state with an exciton in the acceptor and zero exciton in the donor; $\hat{V}_{\text{int}}$ is the exciton Coulomb interaction operator; and $\hbar\omega_{exc}$ is the exciton's energy. As described in Chap. 5 from Understanding and Modeling Förster-type Resonance Energy Transfer (FRET) Vol. 1 (Refs. [2–4]), this expression can be simplified into

$$\gamma_{trans} = \frac{2}{\hbar}\text{Im}\left[\int dV\left(\frac{\varepsilon_{A}(\omega)}{4\pi}\right)\mathbf{E}_{in}(\mathbf{r})\cdot\mathbf{E}_{in}^{*}(\mathbf{r})\right] \tag{3.2}$$

where the integration is taken over the acceptor volume, $\varepsilon_A(\omega)$ is the dielectric function of the acceptor, and $\mathbf{E}_{in}(\mathbf{r})$ includes the effective electric field created by an exciton at the donor side. The electric field is calculated with $\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r})$ and the electric potential $\Phi(\mathbf{r})$ is given by

$$\Phi_{\alpha}(\mathbf{r}) = \left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)\frac{(\mathbf{r}-\mathbf{r}_0)\cdot\hat{\boldsymbol{\alpha}}}{|\mathbf{r}-\mathbf{r}_0|^{3}} \tag{3.3}$$

where ed_{exc} is the dipole moment of the exciton and ε_{eff_D} is the effective dielectric constant of the donor, which depends on the geometry and the exciton dipole direction, $\alpha = x, y, z$. Table 3.1 provides a summary for the donor dielectric constant as calculated for a single donor in Chap. 1 (Ref. [5]).

The average FRET rate (at room temperature) is calculated as

$$\gamma_{trans} = \frac{\gamma_{x,trans}+\gamma_{y,trans}+\gamma_{z,trans}}{3} \tag{3.4}$$

Table 3.1 Effective dielectric constant expressions for the cases of NP, NW, and QW in the long distance approximation

α-direction	NP	NW	QW
x	$\varepsilon_{eff_D} = \frac{\varepsilon_{NP}+2\varepsilon_0}{3}$	$\varepsilon_{eff_D} = \frac{\varepsilon_{NW}+\varepsilon_0}{2}$	$\varepsilon_{eff_D} = \varepsilon_0$
y	$\varepsilon_{eff_D} = \frac{\varepsilon_{NP}+2\varepsilon_0}{3}$	$\varepsilon_{eff_D} = \varepsilon_0$	$\varepsilon_{eff_D} = \varepsilon_0$
z	$\varepsilon_{eff_D} = \frac{\varepsilon_{NP}+2\varepsilon_0}{3}$	$\varepsilon_{eff_D} = \frac{\varepsilon_{NW}+\varepsilon_0}{2}$	$\varepsilon_{eff_D} = \varepsilon_0$

In this table the cylinder main axis is considered to be along the y-direction [Reprinted (adapted) with permission from Ref. [5] (Copyright 2013 American Chemical Society)]

where $\gamma_{\alpha,trans}$ is the transfer rate for the α-exciton ($\alpha = x, y, z$). In the following section the results obtained in Chap. 2 (Ref. [5]) are used to derive expressions for the assembly cases.

3.1 Energy Transfer Rates for Nanoparticle, Nanowire, or Quantum Well to 1D Nanoparticle Assembly

The FRET rate analytical equations are derived in the long distance approximation, when the donor is an NP, an NW, or a QW while the acceptor is a 1D NP assembly (linear chain) (Fig. 3.1). Assuming that the donor size is smaller than the separation distance between the D–A pair and using the long distance approximation, the energy transfer rate $\gamma_{\alpha,i}$ from the donor and the ith NP in the 1D NP assembly (chain) is given by

$$\gamma_{\alpha,i} = \frac{2}{\hbar} b_\alpha \left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \frac{1}{\left(r^2 + y_i^2\right)^3} \tag{3.5}$$

where $b_\alpha = \frac{1}{3}, \frac{1}{3}, \frac{4}{3}$ for $\alpha = x, y, z$, respectively; ed_{exc} is the exciton dipole moment; ε_{eff_D} is the effective dielectric constant for the exciton in the donor given in Table 3.1; ε_0 is the medium dielectric constant; R_{NP_A} and ε_{NP_A} are the acceptor NP radius and dielectric function, respectively; and r is the distance between the donor and linear NP chain (Fig. 3.1). The total transfer from the donor to all acceptor NPs in the chain is

$$\gamma_\alpha = \sum_i \gamma_{\alpha,i} = \frac{2}{\hbar} b_\alpha \left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \sum_i \frac{1}{\left(r^2 + y_i^2\right)^3} \tag{3.6}$$

if the separation between NP is small and a linear density of particle λ_{NP} can be defined, then (3.6) can be rewritten as

$$\gamma_\alpha = \frac{2}{\hbar} b_\alpha \left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \int_{-\infty}^{\infty} \frac{\lambda_{NP}}{\left(r^2 + y^2\right)^3} dy \tag{3.7}$$

After integration, the expression boils down to

$$\gamma_\alpha = \frac{2}{\hbar} b_\alpha \left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2 \left(\frac{3\pi R_{NP_A}^3}{8}\right) \frac{\lambda_{NP}}{d^5} (c_D)^5 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \tag{3.8}$$

where d is the perpendicular distance between the donor and linear NP chain and c_D is a constant, which depends on the donor geometry; $c_D = 1$ for a NP, and $\cos(\theta_0)$ for a QW, and $\left(1 + \tan^2\theta_0 \sin^2\alpha\right)^{-1/2}$ for a NW. θ_0 is the angle between r and d as

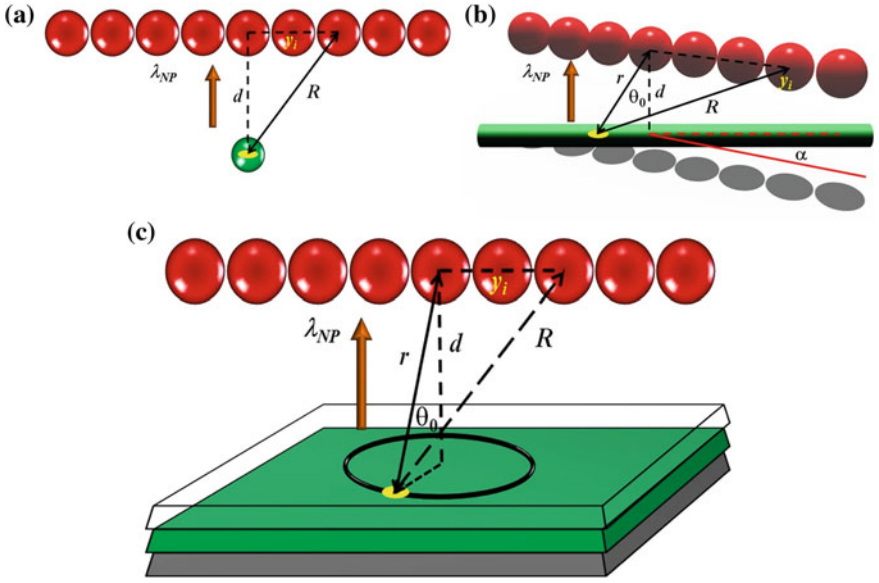


Fig. 3.1 Schematic for the energy transfer of **a** NP → 1D NP assembly, **b** NW → 1D NP assembly, and **c** QW → 1D NP assembly. *Orange arrows* show the energy transfer direction. *Yellow circles* represent an exciton in the α-direction. d is the separation distance. θ_0 is the azimuthal angle between d and r. α is the angle between NW axis and the NP array axis [Reprinted (adapted) with permission from Ref. [1] (Copyright 2014 American Chemical Society)]

shown in Fig. 3.1b, c. α is the angle between NW axis and the NP array axis (Fig. 3.1b). Note that the energy transfer rate distance dependency changes from $\gamma \propto d^{-6}$ to $\gamma \propto d^{-5}$. Furthermore, the FRET rate Eq. (3.8) strongly depends on the angle when the donor is a QW or NW.

3.2 Energy Transfer Rates for Nanoparticle, Nanowire, or Quantum Well to 2D Nanoparticle Assembly

We present simplified expressions for FRET rate in the long distance approximation when the donor is an NP, an NW, or a QW and the acceptor is a 2D NP assembly (plane) (Fig. 3.2). Similar to the previous case, we assume that the donor size is small compared to the D–A separation distance d. The energy transfer from a donor NP to the i, j-th acceptor NP in a 2D assembly is

$$\gamma_{\alpha,i,j} = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 R^3_{NP_A} \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\,|\varepsilon_{NP_A}(\omega)| \frac{1}{\left(d^2 + \rho^2_{i,j}\right)^3} \tag{3.9}$$

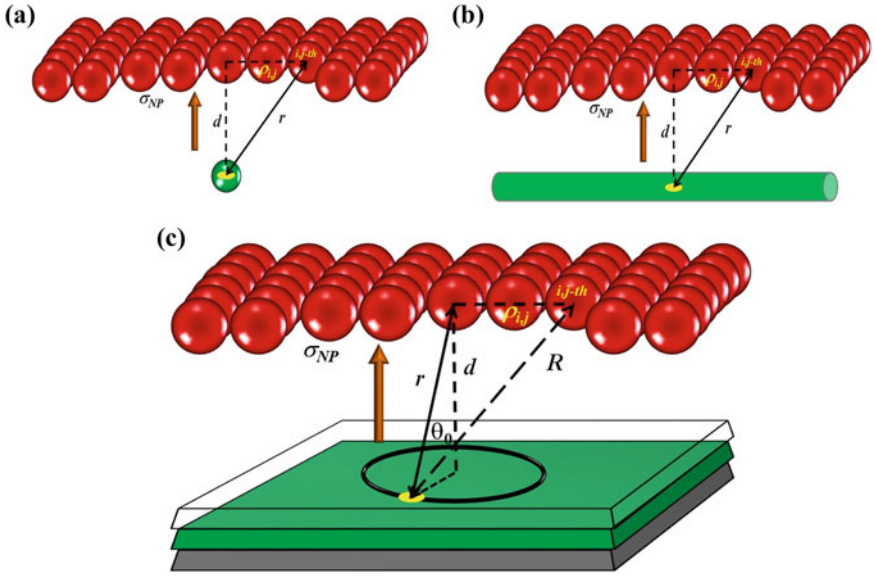


Fig. 3.2 Schematic for the energy transfer of **a** NP → 2D NP assembly, **b** NW → 2D NP assembly, and **c** QW → 2D NP assembly. *Orange arrows* denote the energy transfer direction. *Yellow circles* represent an exciton in the α-direction. d is the separation distance. θ_0 is the azimuthal angle between d and r [Reprinted (adapted) with permission from Ref. [1] (Copyright 2014 American Chemical Society)]

Thus, the total transfer rate is given by

$$\gamma_\alpha = \sum_{i,j} \gamma_{\alpha,i,j} = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \sum_{i,j} \frac{1}{\left(d^2 + \rho_{i,j}^2\right)^3} \tag{3.10}$$

Assuming the separation between the acceptor NP is small and a surface density of particle σ_{NP} can be defined, (3.10) reduces to

$$\gamma_\alpha = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \int_0^\infty \frac{2\pi\sigma_{NP}}{\left(d^2 + \rho^2\right)^3} \rho d\rho \tag{3.11}$$

The final equation for the transfer rate is

$$\gamma_\alpha = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 \left(\frac{\pi R_{NP_A}^3}{2}\right) \frac{\sigma_{NP}}{d^4} \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \tag{3.12}$$

For this case, the distance dependency for the energy transfer rate is proportional to d^{-4}. This derivation is consistent with the previous studies reported in Refs. [6–8].

3.3 Energy Transfer Rates for Nanoparticle, Nanowire, or Quantum Well to 3D Nanoparticle Assembly

The FRET rate expression in the long distance approximation when the donor is an NP, an NW, or a QW while the acceptor is a 3D NP assembly is obtained (Fig. 3.3). In the same spirit as the previous cases, we assume that the donor size is small compared to the D–A separation distance d. The energy transfer from a donor NP to the i, j, k-th acceptor NP in a 3D assembly is

$$\gamma_{\alpha,i,j,k} = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega) + 2\varepsilon_0}\right|^2 \mathrm{Im}\left|\varepsilon_{NP_A}(\omega)\right| \frac{1}{\left(x_{ijk}^2 + y_{ijk}^2 + \left(z_{ijk} + d\right)^2\right)^3} \tag{3.13}$$

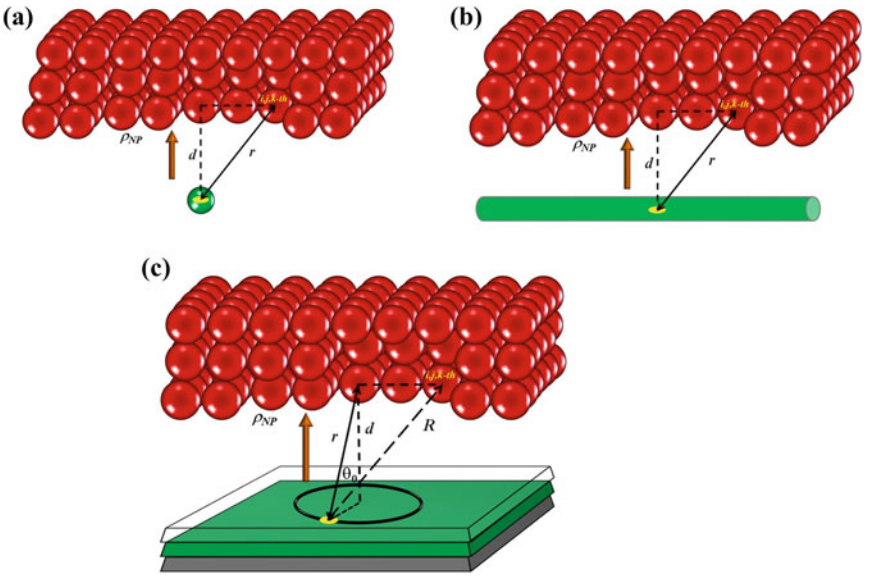


Fig. 3.3 Schematic for the energy transfer of **a** NP → 3D NP assembly, **b** NW → 3D NP assembly, and **c** QW → 3D NP assembly. *Orange arrows* denote the energy transfer direction. *Yellow circles* represent an exciton in the α-direction. d is the separation distance. θ_0 is the azimuthal angle between d and r. [Reprinted (adapted) with permission from Ref. [1] (Copyright 2014 American Chemical Society)]

Thus, the total transfer rate is given by

$$\gamma_\alpha = \sum_{i,j,k} \gamma_{\alpha,i,j,k} = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega)+2\varepsilon_0}\right|^2 \mathrm{Im}\,|\varepsilon_{NP_A}(\omega)| \sum_{i,j} \frac{1}{\left(x_{ijk}^2 + y_{ijk}^2 + \left(z_{ijk}+d\right)^2\right)^3} \tag{3.14}$$

Assuming the separation between the acceptor NPs is small and a volume particle density ρ_{NP} can be defined, (3.10) boils down to

$$\gamma_\alpha = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 R_{NP_A}^3 \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega)+2\varepsilon_0}\right|^2 \mathrm{Im}\,|\varepsilon_{NP_A}(\omega)| \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{\rho_{NP}}{\left(x^2+y^2+(z+d)^2\right)^3} dx dy dz \tag{3.15}$$

The final equation for the transfer rate is obtained as

$$\gamma_\alpha = \frac{2}{\hbar} b_\alpha \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 \left(\frac{\pi R_{NP_A}^3}{6}\right) \frac{\rho_{NP}}{d^3} \left|\frac{3\varepsilon_0}{\varepsilon_{NP_A}(\omega)+2\varepsilon_0}\right|^2 \mathrm{Im}\,|\varepsilon_{NP_A}(\omega)| \tag{3.16}$$

For this case, the distance dependency for the energy transfer rate is proportional to d^{-3}, similar to the bulk case [9].

3.4 Energy Transfer Rates for Nanoparticle, Nanowire, or Quantum Well to 1D Nanowire Assembly

We derive simplified expressions for FRET rate in the long distance approximation when the donor is an NP, an NW, or a QW with the acceptor being a 1D NW assembly (Fig. 3.4). Similar to the previous cases, we consider the energy transfer rate between the donor and the 1D assembly of NWs. In this case, the transfer rate to the i-th NW is

$$\gamma_{\alpha,i} = \frac{2}{\hbar} \left(\frac{e d_{exc}}{\varepsilon_{eff_D}}\right)^2 \left(\frac{3\pi}{32}\right) R_{NW_A}^2 \left(a_\alpha + b_\alpha \left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right) \mathrm{Im}\,|\varepsilon_{NW_A}(\omega)| \frac{1}{(d^2+y_i^2)^{\frac{5}{2}}} \tag{3.17}$$

where $a_\alpha = 0, \frac{9}{16}, \frac{15}{16}$; $b_\alpha = 1, \frac{15}{16}, \frac{41}{16}$ for $\alpha = x, y, z$, respectively; ε_{eff_D} is the effective dielectric constant for the exciton in the donor NP given in Table 3.1; R_{NW_A} is the acceptor NW radius; and d is the distance between the donor and NW assembly (Fig. 3.4). The total transfer from the donor to all acceptor NWs in the chain is

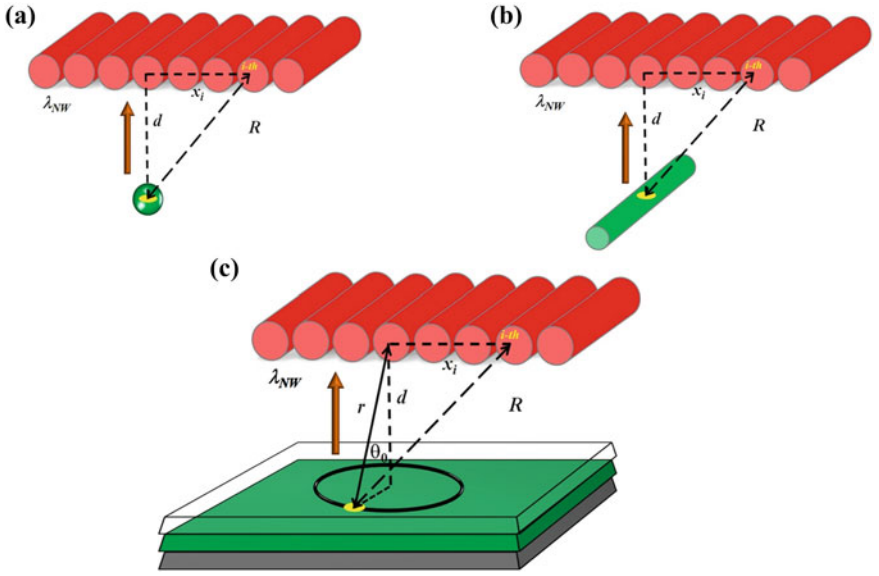


Fig. 3.4 Schematic for the energy transfer of **a** NP → 1D NW assembly, **b** NW → 1D NW assembly, and **c** QW → 1D NW assembly. *Orange arrows* show the energy transfer direction. *Yellow circles* represent an exciton in the α-direction. d is the separation distance. θ_0 is the azimuthal angle between d and r [Reprinted (adapted) with permission from Ref. [1] (Copyright 2014 American Chemical Society)]

$$\gamma_\alpha = \sum_i \gamma_{\alpha,i} = \frac{2}{\hbar}\left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2\left(\frac{3\pi}{32}\right)R_{NW_A}^2\left(a_\alpha + b_\alpha\left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right)\mathrm{Im}\,|\varepsilon_{NW_A}(\omega)|\sum_i \frac{1}{(d^2+y_i^2)^{\frac{5}{2}}} \tag{3.18}$$

Under the assumption that the NWs are close to each other with a linear density λ_{NW},

$$\gamma_\alpha = \frac{2}{\hbar}\left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2\left(\frac{3\pi}{32}\right)R_{NW_A}^2\left(a_\alpha + b_\alpha\left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right)\mathrm{Im}\,|\varepsilon_{NW_A}(\omega)|\int_{-\infty}^{\infty}\frac{\lambda_{NW}}{(d^2+y^2)^{\frac{5}{2}}}dy \tag{3.19}$$

The final result is

$$\gamma_\alpha = \frac{2}{\hbar}\left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2\left(\frac{\pi R_{NW_A}^2}{8}\right)\left(\frac{\lambda_{NW}}{d^4}\right)\left(a_\alpha + b_\alpha\left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right)\mathrm{Im}\,|\varepsilon_{NW_A}(\omega)| \tag{3.20}$$

It is observed that when the NWs are assembled with high density, the distance dependency for the transfer rate changes from d^{-5} to d^{-4}. A similar result can be found in Ref. [10] for the case of NW → 1D NW array.

3.5 Energy Transfer Rates for Nanoparticle, Nanowire, or Quantum Well to 2D Nanowire Assembly

The FRET rate expression in the long distance approximation when the donor is an NP, an NW, or a QW while the acceptor is a 2D NW assembly is presented (Fig. 3.5). In the same way as the previous cases, we consider the energy transfer rate between the donor and the 2D assembly of NWs. In this case, the transfer rate to the *i, j*-th NW is

$$\gamma_{\alpha,i,j} = \frac{2}{\hbar}\left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2\left(\frac{3\pi}{32}\right)R_{NW_A}^2\left(a_\alpha + b_\alpha\left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right)\mathrm{Im}\left|\varepsilon_{NW_A}(\omega)\right|\frac{1}{\left(y_{i,j}^2+\left(d+z_{i,j}\right)^2\right)^{\frac{5}{2}}} \tag{3.21}$$

The total transfer from the donor to all acceptor NWs in the array is

$$\gamma_\alpha = \sum_{i,j}\gamma_{\alpha,i,j} = \frac{2}{\hbar}\left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2\left(\frac{3\pi}{32}\right)R_{NW_A}^2\left(a_\alpha + b_\alpha\left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right)\mathrm{Im}\left|\varepsilon_{NW_A}(\omega)\right|\sum_i\frac{1}{\left(y_{i,j}^2+\left(d+z_{i,j}\right)^2\right)^{\frac{5}{2}}} \tag{3.22}$$

Under the assumption that the NWs are close to each other with a surface density σ_{NW},

$$\gamma_\alpha = \frac{2}{\hbar}\left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2\left(\frac{3\pi}{32}\right)R_{NW_A}^2\left(a_\alpha + b_\alpha\left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right)\mathrm{Im}\left|\varepsilon_{NW_A}(\omega)\right|\int_0^\infty\int_{-\infty}^\infty\frac{\sigma_{NW}}{\left(y^2+(d+z)^2\right)^{\frac{5}{2}}}dydz \tag{3.23}$$

The final result is obtained as follows:

$$\gamma_\alpha = \frac{2}{\hbar}\left(\frac{ed_{exc}}{\varepsilon_{eff_D}}\right)^2\left(\frac{\pi R_{NW_A}^2}{24}\right)\left(\frac{\sigma_{NW}}{d^3}\right)\left(a_\alpha + b_\alpha\left|\frac{2\varepsilon_0}{\varepsilon_{NW_A}(\omega)+\varepsilon_0}\right|^2\right)\mathrm{Im}\left|\varepsilon_{NW_A}(\omega)\right| \tag{3.24}$$

It worth mentioning that when the NWs are assembled into a high density 2D array, the distance dependency for the transfer rate changes from d^{-5} to d^{-3}. This behavior resembles the bulk case.

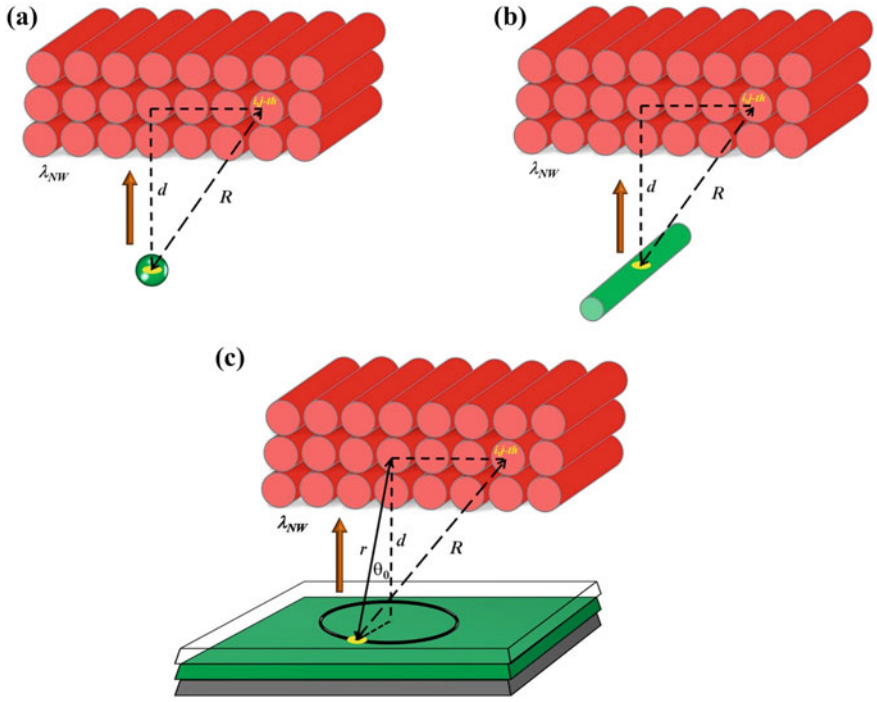
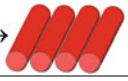
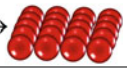
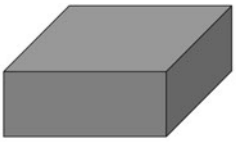
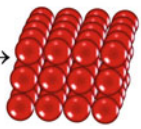
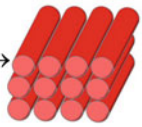


Fig. 3.5 Schematic for the energy transfer of **a** NP → 2D NW assembly, **b** NW → 2D NW assembly, and **c** QW → 2D NW assembly. *Orange arrows* show the energy transfer direction. *Yellow circles* represent an exciton in the α-direction. d is the separation distance. θ_0 is the azimuthal angle between d and r [Reprinted (adapted) with permission from Ref. [1] (Copyright 2014 American Chemical Society)]

3.6 Summary

A summary for all of the derived FRET rates is given in Table 3.2. Table 3.2 lists the transfer rates in the long distance asymptotic behavior in the dipole approximation for all combinations with mixed dimensionality (NP, NW, QW) in all possible arrayed architectures presented in this chapter (1D NP, 2D NP, 3D NP, 1D NW, 2D NW). This table illustrates the functional distance dependency for the FRET rates: (1) when the acceptor is an 1D NP assembly, the FRET rate is proportional to d^{-5} (3.8); (2) when the acceptor is an 2D NP assembly, the FRET rate is proportional to d^{-4} (3.12); when the acceptor is an 3D NP assembly, the FRET rate is proportional to d^{-3} (3.16); (4) when the acceptor is a 1D NW assembly, the FRET rate is proportional to d^{-4} (3.20); and when the acceptor is a 2D NW assembly, the FRET rate is proportional to d^{-3} (3.24). This suggests that the donor dimensionality (NP, NW, QW) does not affect the functional dependency on the distance. In all cases, the FRET rate distance dependence is given by the acceptor

Table 3.2 Generic distance dependency for the FRET rates, with equivalent cases of arrayed nanostructures in term of *d* dependence [Reprinted (adapted) with permission from Ref. [1] (Copyright 2014 American Chemical Society)]

Generic distance dependence	FRET Donor (D) → Acceptor (A)
$\gamma \propto \frac{1}{d^6}$	$X \rightarrow$ 
$\gamma \propto \frac{1}{d^5}$	$X \rightarrow$  $\equiv X \rightarrow$ 
$\gamma \propto \frac{1}{d^4}$	$X \rightarrow$  $\equiv X \rightarrow$  $\equiv X \rightarrow$ 
$\gamma \propto \frac{1}{d^3}$	$X \rightarrow$  $\equiv X \rightarrow$  $\equiv X \rightarrow$ 
$X =$  *d*: separation distance between D and A ≡ : equivalent	

geometry and acceptor array architecture and it is independent of the donor's geometry. Table 3.2 illustrates the FRET rate generic distance dependence with equivalent cases in term of *d* dependence. It is pointing out that the effective dielectric constant depends only on the donor's geometry. Therefore, we can conclude that the FRET's distance dependency is dictated by the confinement degree of the acceptor nanostructure and its stacked array dimensions whereas the donor's confinement affects the modification of effective dielectric constant.

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