<span id="page-0-0"></span>

Contents lists available at [ScienceDirect](www.sciencedirect.com/science/journal/00304018)

# Optics Communications

journal homepage: <www.elsevier.com/locate/optcom>

# The local field dependent effect of the critical distance of energy transfer between nanoparticles



# Chu Viet Ha<sup>a,b</sup>, Do Thi Nga<sup>a</sup>, Nguyen Ai Viet<sup>a</sup>, Tran Hong Nhung<sup>a,\*</sup>

<sup>a</sup> Institute of Physics, Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Viet Nam **b Thai Nguyen University of Education, Thai Nguyen, Viet Nam** 

#### article info

Article history: Received 4 February 2015 Received in revised form 9 April 2015 Accepted 7 May 2015 Available online 8 May 2015

Keywords: Förster resonance energy transfer Dye molecules Fluorescent nanoparticles Gold nanoparticles Localized plasmon coupled surface energy transfer Critical transfer distance

### **ABSTRACT**

The fluorescence resonance energy transfer between various types of fluorophore pairs was investigated. Dye molecules, quantum dots, fluorescent nanoparticles (dye molecules encapsulated in polymer matrices) were used as donor D. Dye molecules and gold nanoparticles were used as acceptor A. We found that the experimental Förster critical transfer distance  $R_0$  is 1–10 nm when both D and A are dye molecules, and becomes larger than 10 nm when the donor is fluorescent nanoparticles. When the acceptors A are gold nanoparticles, the case is considered as localized plasmon coupled nanosurface energy transfer (NSET), the experimental critical distance  $d_0$  increases up to few ten nanometers when D are dye molecules or quantum dots. For the first time, un-expected giant resonance energy transfer (G-RET) phenomenon is observed in our experiments with very large critical transfer distance  $d_0$ , which increases from few ten nanometers to micrometers when the donors are fluorescent and the acceptors are gold nanoparticles. A model "nanowave emitter station and antenna" is given to explain the local field dependence of the critical distance of energy transfer between those nanoparticles. Moreover, a simple theoretical model with size–number contribution (for fluorescent nanoparticles) and surface plasmon coupled enhancement effect (for gold nanoparticles) is proposed to explain these obtained experimental results.

 $\odot$  2015 Elsevier B.V. All rights reserved.

# 1. Introduction

Fluorescence or Förster resonance energy transfer (FRET) has been widely used in biology and chemistry for measuring the distance r between two fluorophores to detect molecular interactions in a number of systems, thanks to their distance-dependent dipole–dipole interaction mechanism. FRET can be used as spectroscopic ruler in various areas such as the interaction of biological molecules in vitro and in vivo assays in cellular research, nucleic acid analysis, signal transduction, light harvesting and metallic nanomaterial etc. Based on the mechanism of FRET a variety of novel chemical sensors and biosensors have been de-veloped [\[1](#page-5-0)–[5\].](#page-5-0) Conventional FRET exhibits the  $R^{-6}$  dependence law of energy transfer rate and characterized by the Förster distance or critical distance  $R_0$ , which defined as the distance at which the energy transfer efficiency is 50%. The  $R_0$  is given by

$$
R_0 = 0.211 \left[ \kappa^2 n^{-4} \phi_{\rm D} J(\lambda) \right]^{1/6} \tag{1}
$$

where  $\phi_D$  is the fluorescence quantum yield of the donor (D) in the absence of the acceptor (A),  $\kappa^2$  is the dipole orientation factor, *n* is the refractive index of the medium, and  $J(\lambda)$  is the spectral overlap integral.  $\kappa^2 = 2/3$  for isotropically oriented dipoles [\[6\].](#page-5-0) The FRET suffers from a limited length scale of approximately 10 nm. On the other hand, there are many works demonstrated the non-Förster distance dependence of energy transfer. Bagchi et al. showed the  $R^{-2}$  dependence rule for electronic excitation transfer (EET) from a segment of polyfluorene to tetraphenylporphyrin. The Förster expression seems to be inappropriate for the condensed-phase systems where donors and acceptors can be closely packed [\[7\].](#page-5-0) The Förster energy transfer is also breaking down when the energy transfer occurs from a dye molecule to a nanometal surface, which was attributed to the surface energy transfer (SET) and follows  $R^{-4}$ distance dependence. This phenomenon was explained by the surface plasmon coupled nonradiative energy transfer [\[8,9\].](#page-5-0) Energy transfer between dye molecules or quantum dots (QDs) – donors and metallic nanoparticles (MNPs) – acceptors demonstrates a longer range energy transfer phenomenon due to the

\* Corresponding author.

<http://dx.doi.org/10.1016/j.optcom.2015.05.015> 0030-4018/© 2015 Elsevier B.V. All rights reserved.

E-mail address: [thnhung@iop.vast.ac.vn](mailto:thnhung@iop.vast.ac.vn) (T. Hong Nhung).

<span id="page-1-0"></span>localized surface plasmon coupled and described by the nanosurface energy transfer (NSET) mechanism. Due to a large difference in donor and acceptor dimensions, the system is considered as a point dipole interacting with an infinite metal surface for small separation distances and large GNPs. The characteristic distance for which the NSET efficiency is 50%, denoted as  $d_0$  and can be calculated by formula of the Persson–Lang model [\[7\]:](#page-5-0)

$$
d_0 = \left[ 0.225 \frac{c^3 \phi_{\rm D}}{\omega_{\rm dye}^2 k_{\rm f} \omega_{\rm f}} \right]^{1/4} \tag{2}
$$

where c is the speed of light in vacuum,  $\phi_D$  is the quantum yield of the donor,  $\omega_{Fluo}$  is the angular frequency for the donor,  $\omega_f$  and  $k_f$  are the Fermi angular frequency and wavevector of metal. It can be seen in formula  $(2)$ , the distance  $d_0$  do not depends on both donor and GNP size. This model of the energy transfer from point dipoles to MNPs has been used to calculate the characteristic distance for single emitter–metallic nanosphere pairs [\[10,11\]](#page-6-0) and for planes of QD–gold nanospheres [\[6,](#page-5-0)[12](#page-6-0)–[14\]](#page-6-0). These works emphasized the influence of localized plasmon field (concentration or size of gold nanoparticles) effects on FRET energy transfer between quantum dots, also the plasmon coupled frequency dependence of this type of energy transfer. Distance dependence of localized plasmon coupled energy transfer was also investigated for rare earth doped and dye doped plasmonic core–shell NPs [\[15\]](#page-6-0). It was found that the interaction distance was observed up to few ten nanometers [\[10](#page-6-0)–[12,16\]](#page-6-0) and NSET model provides only a good qualitative description of the distance dependence of the quenching efficiencies since the measured values were always larger than the predicted ones  $[6,11]$  $[6,11]$ . It can be said that the difference in the calculated and measured values of plasmon coupled energy transfer distance comes mainly from two reasons: (i) the point dipole condition or the dimension difference in donor and acceptor pairs, (ii) the influence of the size of nanoparticles participated in the transfer process. In the case of emitter–metallic nanosphere pairs where both D–A nanoparticles are comparable in size, the point dipole condition will be not satisfied and a big difference in calculated and measured values of characteristic distance  $d_0$  will be expected.

This work presents our results on studies of the energy transfer between various type of donor and acceptor pairs; dye molecules, quantum dots, fluorescent nanoparticles are used as donors D and dye molecules, gold nanoparticles are used as acceptors A. The critical transfer distances  $R_0/d_0$  was calculated and experimental estimated for all cases of D–A type. It was found that the critical transfer distances  $R_0/d_0$  depend on the local field of both donor and acceptor when they cannot be considered as the point dipoles. A large  $d_0$  distance up to micrometer was experimental observed when donors are fluorescent and acceptors are gold nanoparticles. A model "nano-wave emitter station and antenna" is given to explain this phenomenon. A theoretical formalism was introduced to compute the energy transfer rates for the experimental results.

#### 2. Experimental section

The donor and acceptor used for experiments are fluorophores and gold nanoparticles (GNPs). The fluorophores are dye molecules, fluorescent nanoparticles and quantum dots (QDs) (Fig. 1). The Cyanine dyes Cy5 were purchased from Invitrogen. The fluorescent nanoparticles are 100 nm Cy3 orange beads (OBs) (Invitrogen) and laboratory manufactured Rhodamine B (RB) doped silica nanoparticles (RBDSNPs). Each OB contains about  $\sim$ 3000 Cy3 dye molecules. There are about  $\sim$ 4000 RB molecules doped in each 100 nm RBDSNP and  $\sim$  150 RB molecules in 20 nm nanoparticles. The 4 nm CdTe QDs were provided by Institute of Materials Science, VAST. The GNPs were purchased from BB International with 20 nm in size. The energy transfer experiments were carried out for five types of D–A pairs: OBs–Cy5 dyes, Cy5 dyes–GNPs, CdTe QDs–GNPs, RBDSNPs–GNPs and OBs–GNPs ([Table 1](#page-2-0)).

The experiments were realized at room temperature and at 532 nm excitation for mixture of D–A pairs in aqueous solution. The donor concentration was fixed while the acceptor concentration was varied. There was no chemical reaction either aggregation between D–A pairs in solution. Absorption spectra were measured using JASCO-V570–UV–vis–NIR spectrometer. The fluorescence spectra were recorded on a Cary Eclipse spectrofluorometer (Varian). Transmission and scanning electron microscopes (TEM, JEM 1011 and SEM, Hitachi S-480) were used to determine the shape, size of particles. The absorption  $\lambda_{Ab}$  and fluorescence  $\lambda_{Fluo}$  maximum of donors and acceptors, also the quantum yield of donors are listed in [Table 1](#page-2-0).

#### 3. Results and discussion

#### 3.1. Experimental

[Fig. 2](#page-3-0) presents the curves of fluorescence intensity of donor versus acceptor concentration of D–A pairs under investigation, also their absorption and fluorescence spectra for clearing. As can be seen in ([Fig. 2](#page-3-0)a), the addition of Cy5 dye molecules in mixture causes the decrease of OBs fluorescence intensity due to the energy transfer from Cy3 dye molecules (donors) in OBs to Cy5 molecules (acceptors) in solution. Using the Förster theory, we can calculate the characteristic critical transfer distance  $R_0$  according to formula [\(1\)](#page-0-0) using the spectral overlap *J*, and quantum yield  $\phi_D$ .

For all other cases [\(Fig. 2](#page-3-0)b–e), the energy transfer occurs between the fluorophores and GNPs, which are metallic nanoparticles. In theses pairs, the gold nanoparticles can enhance or quench the fluorescence of fluorophores depending upon the relative magnitudes of two energy transfer mechanisms: (i) the plasmonic field enhancement at the fluorophores emission frequencies (plasmon coupled fluorescence enhancement) and (ii) the localized plasmon coupled Förster energy transfer from fluorescent particles to gold particles, which quenches the



Fig. 1. (a, b and d) Transmission electron microscope (TEM) image of OBs, GNPs and CdTeQDs, respectively; (c) scanning electron microscope (SEM) image of RB DSNPs.

<span id="page-2-0"></span>Table 1 The donor–acceptor pairs.

	<b>Donor</b>					Acceptor			
	<b>Type</b>	Size (nm)	$\lambda_{Ab}$ (nm)	$\lambda_{Fluo}$ (nm)	Quantum yield	<b>Type</b>	Size (nm)	$\lambda_{Ab}$ (nm)	$\lambda_{Fluo}$ (nm)
	OBs $(Cy_3$ doped)	100	540	560	0.11	Dye molecules Cy5	$\sim$ 0.3–0.5	640	668
	Dye molecules Cy5	$\sim$ 0.3–0.5	640	668	0.37	GNPs	20	522	<b>NA</b>
	CdTe ODs	$\sim$ 4	566	602	0.3				
4	<b>RBDSNPs</b>	20	554	578	0.45				
		100	554	580	0.35				

fluorescence [\[17\].](#page-6-0) The competition of these mechanisms is depending on the spectral overlap of fluorophores and GNPs, their relative concentration, excitation wavelength. It can be seen from [Fig. 2](#page-3-0)b, the addition of GNPs in the solution of Cy5 molecules causes only the fluorescence quenching, while the interaction between GNPs and CdTe QD, RBDSNPs, or OBs causes both fluorescence enhancement and quenching, depending on the concentration of GNPs in the solution ([Fig. 2](#page-3-0)c–e). In this work, we concentrate on the results of localized plasmon coupled Förster energy transfer; the results on fluorescence enhancement will be discussed in another work. The characteristic distance  $d_0$  of the energy transfer between the fluorofores and GNPs have been calculated by formula [\(2\)](#page-1-0) using quantum yield  $\phi_D$  and central emission frequency  $\omega_{Fluo}$  of the donors. For gold metal,  $\omega_f = 8.4 \times 10^{15} \text{ s}^{-1}$ ,  $k_f = 1.2 \times 10^8 \text{ cm}^{-1}$  [\[16\]](#page-6-0).

On other hand,  $R_0$  and  $d_0$  can be experimental estimated as the average distance of D–A pairs (center-to-center) at acceptor half quenching concentration when  $I_{0d}/I_d$ =2, where  $I_{0d}$  and  $I_d$  is the fluorescence intensity of donor without and with acceptor, respectively.

The critical energy transfer distance for different D–A pairs are presented in [Table 2](#page-4-0). The results show that for the case of OBs–Cy5 molecules,  $R_0$  is calculated  $\sim$  5.0 nm, while the experimental value is 55.0 nm, much larger than the typical Förster transfer distance between two dye molecules. The typical Förster transfer distance between Cy3 and Cy5 molecules is about 5 nm (data not shown).

When the acceptors are GNPs, the experimental values of this distance (denoted as  $d_0$ ) are longer than 10 nm and strongly depend on the type of donors, while the calculated values are little changed and all shorter than 10 nm. For the Cy5 molecules–GNPs pair, the experimental  $d_{0exp}$  is 18.0 nm and increases up to 38.4 nm for CdTe QDs–GNPs pair. These values coincide with the values published in previous works [\[10,11\]](#page-6-0). The giant transfer distance 803, 1161 and 1854 nm is obtained when both D–A are nanoparticles (RBDSNPs–GNPs and OBs–GNPs). As shown in [Table 2,](#page-4-0) for the plasmon coupled cases, the transfer distance  $d_{0exp}$  increases with the size of fluorophore-donors: the bigger donor size, the longer transfer distance. It should be emphasized that when the fluorescent NPs (RBDSNPs and OBs) are the donors, their size (20 and 100 nm) are comparable or even bigger than that of acceptors-GNPs (20 nm), then the NSET model of point-dipole interacting with an infinite metal surface is no longer true. It needs to find a suitable alternative model to explain the received experimental results.

The conventional FRET is the transfer between two dye molecules and is considered as the interaction between two point-dipoles. So, in the Förster theory, the magnitude of the electric field of donor and acceptor is not included. Due to their smallness of the electric dipole local field, the transfer is effective only in the distance  $<$  10 nm. In our experiment, each RBDSNP or OB contains several hundreds to thousands RB or Cy3 molecules, so each RBDSNP or OB is no longer a point but a giant dipole with the electric local field is hundreds or thousands times stronger than that of each Cy5 dye molecule. Therefore, the transfer energy from OBs to Cy5 molecules is the interaction between a big-dipole with a point-dipole, so the magnitude of the electric field of OB-dipoles can affect the interaction distance, making it scaling out.

For the case of the energy transfer between the dye molecules and GNPs, the electric local field of GNP-acceptors is stronger than that of molecular dyes, so they can interact at longer distance than dye molecules-acceptors. As the dye doped nanoparticles (DDNPs)-donors, these plasmon coupled dipole-acceptors cannot be considered as the point-dipoles. The acceptor-dipole field depends on the local plasmon field of GNPs, hence depends on the size of GNPs. When both donor and acceptor are nanoparticles, the energy transfer between them is the interaction between two non-point-dipoles, depending on the magnitude of their local electric field. The electric local field of GNP-acceptor is stronger than that of Cy5 molecular dye-acceptor, so these GNP-dipoles can interact at longer distance than Cy5 dye-dipole. The local field of each CdTeQD-donor is stronger than that of each Cy5 dye molecule-donor, so the CdTe QD-dipole can interact with the GNP-dipole at the distance larger than that of the Cy5 dye point-dipole with the GNP-dipole. The transfer from RBDSNPs or OBs to GNPs is the interaction between two dipoles of giant local field resulting in a much extended distance of transfer. The transfer distance of 100 nm RBDSNPs–GNPs and OBs–GNPs pairs has not the same value. This difference may be explained by the spectral difference and the number of dye molecules entrapped inside the polymer nanoparticles.

The transfer interaction between donor–acceptor pairs in this work can be explained as the interaction between two dipoles with different amplitude of electric field: the higher amplitude or the stronger is the field, the longer is the transfer distance ([Fig. 3\)](#page-4-0). The local field dependence of the critical distance of energy transfer between nanoparticles also described as the working distance of a "wave emitter station and antenna". In this model, the local field of dye molecules, gold and dye doped nanoparticles (DDNPs) is considered as the power of a waver emitter station and antenna. The more powerful station, the longer distance it can emitted its wave. The bigger is the antenna, at the longer distance it can detect the emitter signals. The local field of GNPs and DDNPs is much higher than that of the dye molecules, so their waves can cover a space much bigger than that of dye molecules.

## 3.2. Förster resonance energy transfer (FRET) and nanometal surface energy transfer (NSET) theory

To explain the above model, we introduce a general formalism to compute the FRET and NSET like rates for D–A systems. This formalism includes a particular case of the standard Förster theory and gives a simple explanation the experimental results in previous part. Consider a donor (emitter) and acceptor (absorber) with spherical shape, arbitrary locations and orientations of transition dipoles, as illustrated in [Fig. 3.](#page-4-0)

Denote by  $(\vec{r}_A, \vec{G}_A)$  and  $(\vec{r}_B, \vec{G}_D)$  the position and direction of the effective transition dipole of the acceptor and donor, respectively.

<span id="page-3-0"></span>

Fig. 2. Absorption, fluorescence spectra (left) and donor fluorescence intensity vs. acceptor concentration of D–A pairs (right): (a) OBs–Cy5 dyes, (b) Cy5 dyes–GNPs, (c) CdTeQDs–GNPs, (d) RBDSNPs 20 and 100 nm–GNPs and (e) OBs–GNPs.

<span id="page-4-0"></span>![](_page_4_Picture_657.jpeg)

![](_page_4_Picture_658.jpeg)

For electric-dipole transition (El–El transfer), the normalized FRET rate  $k = I_{DA}/I_0$  can be calculated by electric Green function method [\[18\]](#page-6-0):

$$
k = I_{DA}/I_0 = 18\pi\epsilon_0^2 c^4 \int_0^\infty \frac{d\omega}{\omega^4} f_D(\omega) f_A(\omega) M(\omega),
$$
 (3)

where *ΓDA* is the energy transfer rate from donor to acceptor, *Γ*<sup>0</sup> is the decay rate of donor in the absence of acceptor, *ω* is the emission frequency,  $c$  is the speed of light,  $f_{\!\scriptscriptstyle D} \left( \omega \right)$  and  $f_{\!\scriptscriptstyle A} \left( \omega \right)$  are the normalized emission spectrum of the donor and acceptor, respectively. Denote by  $D(\vec{A}, \vec{b}; \omega)$  is the Green function, the function M is

$$
M(\omega) = \left| \overrightarrow{G}_D(\omega), D(\overrightarrow{r}_A, \overrightarrow{r}_D; \omega), \overrightarrow{G}_A(\omega) \right|^2, \tag{4}
$$

and expressed by a Feynman diagram in Fig. 4 with vertex parts *GA* , *GD* , and dressed photon propagator (Green function) *D*.

Using a some kinds of unified theory, we have [\[19\]](#page-6-0)

$$
M(\omega) = \frac{1}{(4\pi\varepsilon_0)^2} K^2 G_A(\omega)^2 G_D(\omega)^2 \frac{1}{R^6} \Big[ 3 + (\omega R/c)^2 + (\omega R/c)^4 \Big],
$$
 (5)

where  $K^2$  is the orientation factor of effective dipoles and can take values from 0 (perpendicular transition effective dipoles) to 1 (parallel transition effective dipoles), and  $R = \begin{bmatrix} \vec{r}_A - \vec{r}_D \end{bmatrix}$  is the distance between the acceptor and the donor.

The first term of Eq. (5) gives the standard Förster  $R^{-6}$  distance depending law with virtual photon (radiationless transfer, dominate at very low frequency), while the third term leads to the  $R^{-2}$ 

![](_page_4_Figure_12.jpeg)

Fig. 4. The Feynman diagrams for fluorescence resonance energy transfer of a donor fluorophore (D) and a nearby acceptor fluorophore (A).

law of Coulomb (radiative transfer, dominate at very high frequency). Because both donor and acceptor have spherical shape, the second term has a  $R^{-4}$  law in unified theory is reasonably considered due to the surface plasmon contribution (partly radiationless and partly radiative transfer, dominate at medium frequency). In the low and medium frequency range, neglecting the third term of (5), the rate now is  $k = k_F + k_{SP}$  with Förster (fluorescence) like  $k_F = \frac{F}{F} / F_0$ , and surface plasmon (SP) like  $k_{SP} = F_{SP}/F_0$  parts. Considering vertex parts  $G_A(\omega)$  and  $G_D(\omega)$ are low varying functions compare with spectral functions  $f_A(\omega)$  and  $f_D(\omega)$ , we can bring them out from integral and give some average value. For the case of FRET like

$$
k_F = \frac{F}{F_0} \left( \frac{R_{0F}}{R} \right)^6, \tag{6}
$$

![](_page_4_Figure_16.jpeg)

Fig. 3. Model "wave emitter station and antenna".

<span id="page-5-0"></span>with the Förster radius

$$
R_{0F}^{6} = 3CK^{2}G_{AF}^{2}G_{DF}^{2}J_{F}, \qquad (7)
$$

where  $C = 9/(8\pi)$  is a constant,  $G_{AF}$  and  $G_{DF}$  are vertex parts, and  $J_F = c^4 \int_0^\infty \frac{d\omega}{\omega^4} f_D(\omega) f_A(\omega)$  is the D–A spectral overlap integral of FRET-like mechanism.

In the case of NSET like

 $k_{SP} = I_{SP} / I_0 \sim (R_{0SP}/R)^4,$  (8)

the in-spirit Förster radius can be defined as follows:

$$
R_{0SP}^4 = CK^2 G_{ASP}^2 G_{DSP}^2 J_{SP}
$$
\n(9)

where *G<sub>ASP</sub>* and *G<sub>DSP</sub>* are vertex parts, and  $\int_{SP} = c^2 \int_0^\infty \frac{d\omega}{\omega^2} f_D(\omega) f_A(\omega)$ ∞ is the D-A spectral overlap integral of NSET-like mechanism. Note that, in the case of NSET with a gold nanoparticle acceptor, the  $R^{-4}$ distance dependence is observed for large particles [2[,20\].](#page-6-0)

For the case of standard FRET with two molecular dyes, we take the vertex parts as dipole moment of atoms  $\vec{\mu}_A$ ,  $\vec{\mu}_D$ , the standard Förster radius is

$$
R_0^6 = 3CK^2\mu_A^2\mu_D^2J_0,\tag{10}
$$

and generally in the range 1–10 nm, here *J* <sup>0</sup> is the standard spectral overlap integral.

From the structure of the Feynman diagram in [Fig. 4,](#page-4-0) it is easy to see that enhancement might came from the vertex parts (depending on the properties of D, A and environment) or propagator part (depending only on transfer photon and environment, which characterized by a dielectric constant of media). Assume the energy transfer between donor and acceptor do not change the environment in which photon propagated, then the enhancement just came from the vertex parts only. We introduce the vertex enhancement factors  $n_i$ ,  $i = F$ , SP by definition

$$
\eta_i = \eta_{Ai} \eta_{Di} = \left(\frac{G_{Ai}^2}{\mu_A^2}\right) \left(\frac{G_{Di}^2}{\mu_D^2}\right). \tag{11}
$$

Assume that the spectral overlap integrals *J <sup>F</sup>* and *J* <sup>0</sup> are in the same order, we have

$$
\left(\frac{R_{0F}}{R_0}\right)^6 \approx \eta_F, \quad \left(\frac{R_{0SP}}{R_0}\right)^4 \approx \eta_{SP}\left(\frac{J_{SP}}{J_0}\right)R_0^2\tag{12}
$$

In the case of spherical GNPs acceptor  $G_{Au} \approx ga^{3/2}/\lambda_P^{1/2}$ , where a is the radius, *λ<sup>P</sup>* is the plasmon wavelength, and g is defined as  $g = (g_n - g_{out})/(\epsilon_n + 2\epsilon_{out})$ , here  $\epsilon_n$  is the dielectric constant of the metal nanoparticle, and *εout* is the dielectric constant of external environment [\[17,18\].](#page-6-0) The maximum g-enhancement occurs when the denominator of g approaches zero ( $\epsilon_{in} \approx -2\epsilon_{out}$ ) and typically  $g \sim 10-10^2$ . The radius of GNPs usually is taken in the range 5– 100 nm, thus the *a*-enhancement is about  $10<sup>2</sup>$ . Thus the GNP-enhancement  $\eta_{AF} \sim 10^6 - 10^8$ .

For the case of fluorescent nanoparticle donor with the size 10– 100 nm containing several thousand molecular dyes, for example  $N=3400$  in 100 nm silica NPs, beside that the local field also in-<br>creased by the Claussius–Mossotti relation, so Claussius–Mossotti  $\eta_{\text{DF}} = (G_{\text{DF}}/\mu_{\text{D}})^2 \sim N^2 \sim 10^7 - 10^8$ .

Taking into account together the total enhancement factor  $r_F \sim 10^{13} - 10^{16}$ , we estimate that  $R_{0F}/R_0 \sim 10^2 - 5.10^2$ , thus the Förster radius of FRET-like mechanism *R*0*<sup>F</sup>* can reach to μm scale. This result can be applied to explain the experimental value  $R_0$ =55.0 nm of OB–Cy5 molecule pair on our experiment.

To estimate the Förster radius of NSET-like mechanism *R*0*SP*, considering  $J_{SP} \approx c^2 \omega_{max}^2 \int_0^\infty \frac{d\omega}{\omega^4} f_D(\omega) f_A(\omega) = J_{0F} / \lambda_{max}^2$ , where  $\omega_{max}$ 

and *λ*max is the maximal frequency and wavelength of transition, we have

 $(R_{0SP}/R_0)^4 \approx r_{\text{SP}} R_0^2 f_{\text{SP}} / J_0 \sim (1/3) (R_0/\lambda_{\text{max}})^2 r_F \sim 10^{-5} r_F \sim 10^8 - 10^{11}$ that  $R_{0SP}/R_0 \sim 10^2 - 6.10^2$  as the same order of  $R_{0F}/R_0$ . We note here both *R*0*<sup>F</sup>* and *R*0*SP* can reach to μm scale but NSET-like mechanism can give greater transfer distance due to the  $R^{-4}$  law as observed on our experiments. This theory results can explain the experimental giant transfer distance observed in our experiment.

#### 4. Conclusion

The FRET and NSET critical transfer distances  $R_0$  and  $d_0$  between various type of D–A fluorophore pairs have been investigated, where dye molecules, quantum dots and fluorescent nanoparticles are donor D, dye molecules and gold nanoparticles are acceptor A. When D is fluorescent nanoparticles and A is dye molecules, the experimental value of  $R_0$  is larger than 10 nm. The experimental value of  $d_0$  is few ten nanometers when dye molecules or quantum dots are donors and gold nanoparticles are acceptors. For the first time, a giant distance energy transfer phenomenon has been observed with very large critical transfer distance reached to micrometers when dye doped nanoparticles are donors and gold nanoparticles are acceptors. The model "wave emitter station and antenna" is given to explain the local field dependence of the critical distance of energy transfer between nanoparticles. The theoretical compute shows that the critical distance of both FRET like and NSET like cases can reach to μm scale when the total enhancement factor  $\eta_F \sim 10^{13} - 10^{16}$ . Other experimental and theoretical works should be carried out to clarify this giant distance of resonance energy transfer. The obtained results can be used for photonic and biophotonic applications.

#### Acknowledgments

This work was supported by the National Project No.01/2/2011/ HD-NCCBUD.

### References

- [1] B. Valeur, Molecular Fluorescence Principles and Applications, Wiley-VCH, New York (2001) <http://dx.doi.org/10.1002/3527600248> (accessed 09.08.14; Online service).
- [2] T. Gulin-Sarfraz, J. Sarfraz, D.Ş. Karaman, J. Zhang, C. Oetken-Lindholm, A. Duchanoy, et al., FRET-reporter nanoparticles to monitor redox-induced intracellular delivery of active compounds, RSC Adv. 4 (2014) 16429–16437, [http://dx.doi.org/10.1039/C4RA00270A.](http://dx.doi.org/10.1039/C4RA00270A)
- [3] E. Yaghini, F. Giuntini, I.M. Eggleston, K. Suhling, A.M. Seifalian, A.J. MacRobert, Fluorescence lifetime imaging and FRET-induced intracellular redistribution of tat-conjugated quantum dot nanoparticles through interaction with a phthalocyanine photosensitiser, Small 10 (2014) 782–792, [http://dx.doi.org/10.1002/](http://dx.doi.org/10.1002/smll.201301459) [smll.201301459](http://dx.doi.org/10.1002/smll.201301459).
- [4] Y. Fu, J. Zhang, J.R. Lakowicz, Plasmon-Controlled Fluorescence: Applications to Sensing and Single Molecule Detection, in: A. Periasamy, P.T.C. So, K. König (Eds.), 2010, pp. 756903–756906, [http://dx.doi.org/10.1117/12.850765.](http://dx.doi.org/10.1117/12.850765)
- J. Asselin, M.L. Viger, D. Boudreau, Metal-enhanced fluorescence and FRET in multilayer core–shell nanoparticles, Adv. Chem. 2014 (2014) e812313, [http:](http://dx.doi.org/10.1155/2014/812313) [//dx.doi.org/10.1155/2014/812313](http://dx.doi.org/10.1155/2014/812313).
- [6] X. Zhang, C.A. Marocico, M. Lunz, V.A. Gerard, Y.K. Gun'ko, V. Lesnyak, et al., Wavelength, concentration, and distance dependence of nonradiative energy transfer to a plane of gold nanoparticles, ACS Nano 6 (2012) 9283–9290, [http:](http://dx.doi.org/10.1021/nn303756a) [//dx.doi.org/10.1021/nn303756a.](http://dx.doi.org/10.1021/nn303756a)
- [7] K.F. Wong, B. Bagchi, P.J. Rossky, Distance and orientation dependence of excitation transfer rates in conjugated systems: beyond the Förster theory, J. Phys. Chem. A 108 (2004) 5752–5763, [http://dx.doi.org/10.1021/jp037724s.](http://dx.doi.org/10.1021/jp037724s)
- [8] B.N.J. Persson, N.D. Lang, Electron–hole-pair quenching of excited states near a metal, Phys. Rev. B 26 (1982) 5409–5415, [http://dx.doi.org/10.1103/](http://dx.doi.org/10.1103/PhysRevB.26.5409) [PhysRevB.26.5409.](http://dx.doi.org/10.1103/PhysRevB.26.5409)
- [9] [H. Singh, B. Bagchi, Non-Förster distance and orientation dependence of en](http://refhub.elsevier.com/S0030-4018(15)00390-9/sbref9)ergy transfer and applications of fl[uorescence resonance energy transfer to](http://refhub.elsevier.com/S0030-4018(15)00390-9/sbref9)

<span id="page-6-0"></span>[polymers and nanoparticles: How accurate is the spectroscopic ruler with 1/](http://refhub.elsevier.com/S0030-4018(15)00390-9/sbref9) [R6 rule? Curr. Sci. 89 \(2005\) 1710.](http://refhub.elsevier.com/S0030-4018(15)00390-9/sbref9)

- [10] T.L. Jennings, M.P. Singh, G.F. Strouse, Fluorescent lifetime quenching near  $d=1.5$  nm gold nanoparticles: probing NSET validity, J. Am. Chem. Soc. 128 (2006) 5462–5467, <http://dx.doi.org/10.1021/ja0583665>.
- [11] T. Pons, I.L. Medintz, K.E. Sapsford, S. Higashiya, A.F. Grimes, D.S. English, et al., On the quenching of semiconductor quantum dot photoluminescence by proximal gold nanoparticles, Nano Lett. 7 (2007) 3157–3164, [http://dx.doi.org/](http://dx.doi.org/10.1021/nl071729+)  $10.1021/n$  $10.1021/n$  $10.1021/n$  $1071729 +$
- [12] R.G. West, S.M. Sadeghi, Enhancement of energy transfer between quantum dots: the impact of metallic nanoparticle sizes, J. Phys. Chem. C 116 (2012) 20496–20503, [http://dx.doi.org/10.1021/jp305910j.](http://dx.doi.org/10.1021/jp305910j)
- [13] M. Lunz, X. Zhang, V.A. Gerard, Y.K. Gun'ko, V. Lesnyak, N. Gaponik, et al., Effect of metal nanoparticle concentration on localized surface plasmon mediated Förster resonant energy transfer, J. Phys. Chem. C. 116 (2012) 26529–26534, http://dx.doi.org/10.1021/jp309660
- [14] T. Ozel, P.L. Hernandez-Martinez, E. Mutlugun, O. Akin, S. Nizamoglu, I.O. Ozel, et al., Observation of selective plasmon–exciton coupling in nonradiative energy transfer: donor-selective versus acceptor-selective plexcitons, Nano Lett. 13 (2013) 3065–3072, <http://dx.doi.org/10.1021/nl4009106>.
- [15] W. Ge, X.R. Zhang, M. Liu, Z.W. Lei, R.J. Knize, Y. Lu, Distance dependence of

gold-enhanced upconversion luminescence in Au/SiO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> :Yb<sup>3+</sup>, Er<sup>3+</sup> nanoparticles, Theranostics 3 (2013) 282–288, [http://dx.doi.org/10.7150/](http://dx.doi.org/10.7150/thno.5523) [thno.5523.](http://dx.doi.org/10.7150/thno.5523)

- [16] C.S. Yun, A. Javier, T. Jennings, M. Fisher, S. Hira, S. Peterson, et al., Nanometal surface energy transfer in optical rulers, breaking the FRET barrier, J. Am. Chem. Soc. 127 (2005) 3115–3119, <http://dx.doi.org/10.1021/ja043940i>.
- [17] J.R. Lakowicz, Radiative decay engineering 5: metal-enhanced fluorescence and plasmon emission, Anal. Biochem 337 (2005) 171–194, [http://dx.doi.org/](http://dx.doi.org/10.1016/j.ab.2004.11.026) [10.1016/j.ab.2004.11.026](http://dx.doi.org/10.1016/j.ab.2004.11.026).
- [18] R. Vincent, R. Carminati, Magneto-optical control of Förster energy transfer, Phys. Rev. B 83 (2011) 165426, <http://dx.doi.org/10.1103/PhysRevB.83.165426>.
- [19] D.L. Andrews, D.S. Bradshaw, Virtual photons, dipole fields and energy transfer: a quantum electrodynamical approach, Eur. J. Phys. 25 (2004) 845, <http://dx.doi.org/10.1088/0143-0807/25/6/017>.
- [20] C.J. Breshike, R.A. Riskowski, G.F. Strouse, Leaving Förster resonance energy transfer behind: nanometal surface energy transfer predicts the size-enhanced energy coupling between a metal nanoparticle and an emitting dipole, J. Phys. Chem. C. 117 (2013) 23942–23949, [http://dx.doi.org/10.1021/](http://dx.doi.org/10.1021/jp407259r) [jp407259r](http://dx.doi.org/10.1021/jp407259r).