Simple Model for Gold Nano Particles Concentration Dependence of Resonance Energy Transfer Intensity

Simple Model for Gold Nano Particles Concentration Dependence of Resonance Energy Transfer Intensity

N M Hoa[1], C V Ha[2], D T Nga[3], N T Lan[3], T H Nhung[3] and N A Viet[3]

[1] Hue University of Medicine and Pharmacy, Hue, Viet Nam
[2] Thai Nguyen University of Education, Thai Nguyen, Vietnam
[3] Institute of Physics, Vietnam Academy of Science and Technology, Ha Noi, Vietnam

Email: minhhoa2806@gmail.com

Abstract. Gold nano particles (GNPs) concentration dependence of the energy transfer occurs between the fluorophores and GNPs is investigated. In the case of theses pairs, GNPs 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 Forster energy transfer from fluorescent particles to gold particles, which quenches the fluorescence. The competition of these mechanisms is depending on the spectral overlap of fluorophores and GNPs, their relative concentration, excitation wavelength. Simple two branches surface plasmon polariton model for GNPs concentration dependence of the energy transfer is proposed. The experimental data and theoretical results confirm our findings.

1. Introduction

Fluorescence or Forster resonance energy transfer (FRET) has been widely used in biology and chemistry for measuring the distance or between two fluorophores to detect molecular interaction 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. In vivo assays in cellular research, nucleic acid analysic, signal transduction, light harvesting and metallic nanometarial etc. based on the mechanism of FRET a variety of novel chemical sensors and biosensors have been developed [1-14].

FRET is a distance dependent radiationless transfer energy from an excited donor fluorophore to a suitable acceptor through long-range Coulomb dipole-dipole interactions. There are few criteria must be replaced satisfied with met in order for FRET to occur: overlap between emission spectrum of donor (D) and absorption spectrum of acceptor (A), removed it parallel dipole orientations of D and A, suitable fluorescence lifetime of D, and suitable D-A separation (typically up to 10 *nm*).

Forster showed that the efficiency of traditional FRET process is on the inverse sixth power of the distance between D and A pair (or distance dependence of traditional FRET mechanism). Recent experiment argue that the Resonance Energy transfer (RET) between donor and metallic nanoparticle acceptor more look like the energy transfer to a metallic surface (dipole- Surface Energy Transfer (SET)) with the inverse four power of the distance between D and A pair (or distance dependence of SET mechanism) [3-4].

On the other hand, there are many works that demonstrated the non-Forster 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 Forster expression seems to be inappropriate for the condensed phase systems where D and A can be closely packed [7].

In the our previous work [16] we studied the energy transfer between various type of D and A pairs; dye molecules, quantum dots (QDs), fluorescent nanoparticles are used as D and dye molecules, gold nanoparticles (GNPs) are used as A. For the first time, It is observed by experiments un-expected giant resonance energy transfer (Gi-RET) phenomenon is observed by experiments with very large critical transfer distance d_0, which increases from few ten nanometers to micrometers when donors are fluorescent and acceptors are GNPs. It was found that the critical transfer distances depends on the local field of both donor and acceptor when they cannot be considered as the point dipoles.

Additionally the conventional only quenching intensity depending on the concentration of GNPs in the solution, the unconventional with both fluorescence enhancement and quenching depending on the concentration of GNPs is observed. This effect plays an important role in the un-expected Gi-RET phenomenon. A model "nano-wave emitter station and antenna" is given to explain this phenomenon, but it has some limitations for explaining other experimental results.

In this work GNPs concentration dependence of the energy transfer occurs between the fluorophores and GNPs is investigated. When explaining the observed unconventional with both fluorescence intensity enhancement and quenching depending on the concentration of GNPs, a simple two branches surface plasmon polariton model is proposed. Our theoretical results has a good agreement with experimental studies.

2. The experimental result

D and A used for experiments are fluorophores and GNPs. The fluorophores are dye molecules, fluorescent nanoparticles and QDs (Fig.1). The Cyanine dyes (Cy5) weoe 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 ~ 3000 Cy3 dye molecules. There are about ~ 4000 RB molecules doped in each 100 *nm* RBDSNP and ~ 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.
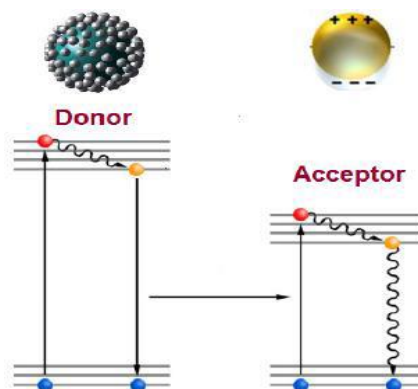

Figure 1. The Forster resonance energy transfer between the fluorophores and gold nano particles.

Fig.1 presents the energy transfer occurs between the fluorophores and GNPs, which are metallic nanoparticles. In theses pairs, the GNPs can enhance or quench the fluorescence of fluorophores depending upon the relative magnitudes of two energy transfer mechanisms: the plasmonic field enhancement at the fluorophores emission frequencies (plasmon coupled fluorescence enhancement); and the localized plasmon coupled Forster energy transfer from fluorescen particles to gold particles, which quenches the fluorescence [18].

The experiments were conducted 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 competition of these mechanisms is depending on the spectral overlap of fluorophores and GNPs, their relative concentration, and excitation wavelength. It can be seen from Fig.2(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 (a), (b)). We concentrate on the results of localized plasmon coupled Förster energy transfer, the results on fluorescence enhancement will be discussed in next part.
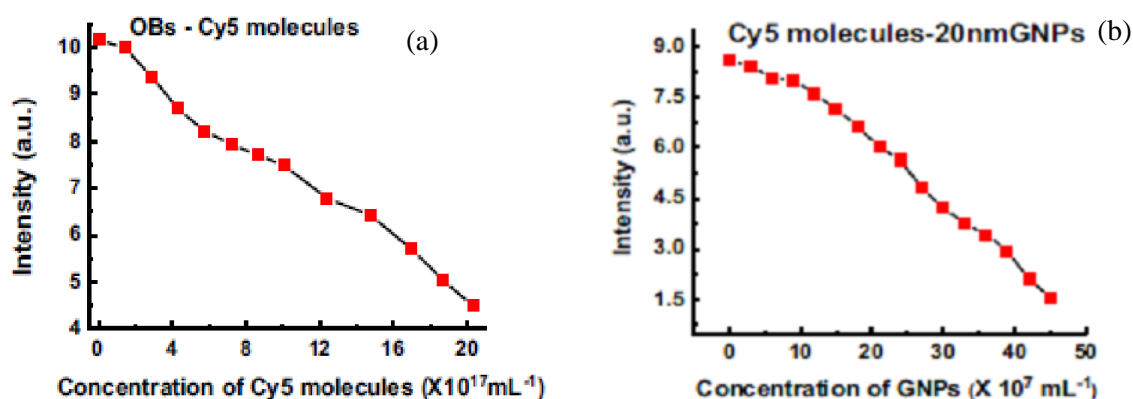
Figure 2. Conventional fluorescence quenching depending on the concentration of GNPs.

Unconventional fluorescence enhancement and quenching depending on the concentration of GNPs and spectrum overlap are presented in the figure 3 in the left, and right correspondingly.
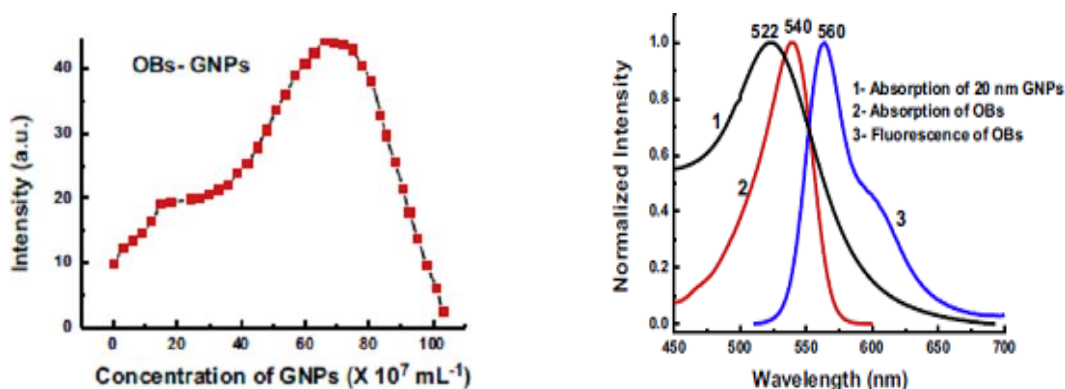
Figure 3. Unconventional fluorescence enhancement and quenching depending on the concentration of GNPs (left), and spectrum overlap (right).

3. FRET, SET and Coulomb energy transfer (CET) mechanisms

Conventional FRET (Fig.2) is a distance dependant radiationless transfer energy from an excited donor fluorophore to a suitable acceptor through long-range Coulomb dipole-dipole interactions. There are few criteria must be satisfied in order to FRET to occur: overlap between emission spectrum of D and absorption spectrum of D, approximately parallel dipole orientations of D and A, suitable fluorescence lifetime of D, and suitable D-A separation (typically up to 10 *nm*).

Forster showed that the efficiency of traditional FRET process is on the inverse sixth power of the distance between D and A pair (or distance dependence of traditional FRET mechanism). Denoting R is distance between D and A, the FRET efficiency E_{FRET} is given by

$$E_{FRET} = \frac{1}{1+\left(R/R_{FRET}\right)^6},$$ (1)

where R is the distance between D and A, R_{FRET} is the Forster radius.

Recent experiment argue that the RET between D and metallic nanoparticle A more look like the energy transfer to a metallic surface (dipole-surface energy transfer) with the inverse four power of the distance between D and A pair (or distance dependence of SET mechanism) [3-4]. The SET efficiency E_{SET} is defined by the expression

$$E_{SET} = \frac{1}{1+\left(R/R_{SET}\right)^4},$$ (2)

where R_{SET} is the SET radius.

In additional, for surface plasmon problem in the literature there are exist one more energy transfer mechanism – CET mechanism by radiate plasmon. In analogy the FRET and SET cases, the CET efficiency E_{CET} is defined by the expression

$$E_{CET} = \frac{1}{1+\left(R/R_{CET}\right)^2},$$ (3)

where R_{CET} is the CET radius.

At $R = R_{FRET}$, R_{SET}, and R_{CET}, half of excitation energy of D is transferred to nano metallic particle A. The energy transfer rate k_E approximately is a product $k_E \approx G_D G_A$ of the interaction elements of the donor G_D and acceptor G_A [15, 16]. These interaction elements can be simplified such that their separation distance d dependencies are some functions of their geometric arrangement. For single dipoles $G \approx \frac{1}{d^3}$, for a 2D dipole array $G \approx \frac{1}{R}$, and for a 3D dipole array $G \approx const$, such that the power of the distance factor decreases as the dimension increases. In the case of FRET, which consists of two single dipoles, is easily derived from this rule such that

$$k_{FRET} \approx G_D G_A \approx G_{Dipole} G_{Dipole} \approx \left(1/R^3\right)\left(1/R^3\right) \approx 1/R^6,$$ (4)

alternatively, FRET is commonly written as $k_{FRET} \approx \left(1/\tau_D\right)\left(R_0/R\right)^6$.

Using a similar formalism, the rate of energy transfer from a dipole to a metallic surface is described interband transition, which was further extended to the conduction electrons in metals, that SET rate is

$$k_{SET} \approx G_D G_A \approx G_{Dipole} G_{Surf} \approx \left(1/R^3\right)\left(1/R\right) \approx 1/R^4.$$ (5)

The CET rate is

$$k_{CET} \approx G_D G_A \approx G_{Surf} G_{Surf} \approx \left(1/R\right)\left(1/R\right) \approx 1/R^2.$$ (6)

Thus, energy transfer to a surface follows a very different distance trend and magnitude of interaction.

4. General resonance energy transfer (GRET) mechanism

The RET mechanism from general donor and general acceptor in the water which investigate in modern theoretical and experimental works still quite complicate and unclear. The interaction of fluorophores with metal surfaces is different depending on the distance regime [1]. For example the interaction of fluorophores with metal surfaces at very close distances (~1nm): radiative rate enhancement is observed; at intermediate distances (~30 *nm*): energy transfer is the dominant process; and at very large distances (50 *nm*): fluorescence oscillations due to the fact that dipole-mirror effects take precedence.

The rate of EET from a fluorescent dye molecule to the surface plasmonic modes of a spherical metal nanoparticle is studied in [S. Bhowmick] where theoretical predicted that the distance dependence of

the transfer rate to vary as R^{-x}, with G_A at intermediate distances, in partial agreement with the recent experimental results, the Forster's R^{-6} dependence is recovered at large separations.

In the work [7] the R^{-2} dependence rule for CET from a segment of polyfluorene to tetraphenylporphyrin was showed. The RET character also depends on size of general D and general A. Based on analyze the recently obtained experimental data [15] we concluded in [17] that RET from fluorescent dipole donor to metal nanoparticle acceptor is like FRET R^{-6} for small radius and like SET R^{-4} for larger radius. For the GNPs the transition radius R_C is quite small ($R_C \sim 1.5\ nm$), for a gold particle with radius smaller 1.5 nm is FRET-like, but larger that is SET-like. We supposed a new reasonable model with mixing mechanism: continue changing from FRET-mechanism for small size to SET-mechanism for large size metal nanoparticles.

Yet no single theoretical model has been explaining and cleaning which the distance dependence in actual is inverse four or six order or some other order? Some questions are raised: what mechanism observed in experiment FRET or SET or CET?, and how distinguish them?

So that a GRET mechanism is considered. The quantum efficiency of energy transfer E_{GRET} can be written as

$$E_{GRET}(R, y) = \frac{1}{1 + (R / R_G)^x}, \tag{7}$$

where R_{GRET} is the general Forster-like radius for general mechanism, x is some positive number describing the inverse order power of the general donor-acceptor pair distance.

The GRET transfer rate is

$$k_{GRET} \approx G_D G_A \approx 1 / R^x, \tag{8}$$

at $R = R_{GRET}$, half of excitation energy of the general donor is transferred to the general acceptor.

Using unitless system $d = R / R_{GRET}$ and denote $\eta_i^{-1} = R_i / R_{GRET}$, where $i =$ FRET, SET, CET, GRET is the number characterized the partial mechanism, we introduce the unitless general the quantum efficiency $E_{GRET}(d, x, \eta_i)$ of energy transfer as

$$E_{GRET}(d, x, \eta_i) = \frac{1}{1 + (\eta_i d)^x}, \tag{9}$$

half of excitation energy of general donor is transferred to general acceptor at d_i, which satisfies the condition $d_i \eta_i = 1$. It is easy to see that $E_{FRET}(d) = E_{GRET}(d, 6, \eta_{FRET})$, $E_{SET}(d) = E_{GRET}(d, 4, \eta_{SET})$, $E_{CET}(d) = E_{GRET}(d, 2, \eta_{CET})$ for simplicity we put $\eta_i = 1$, the behavior of function $E_i(d, x, \eta_i)$, and their derivation $DE_i(d, x, \eta_i) = \partial E(d, x, \eta_i) / \partial d$ are presented in the figure 4 (a and b), for FRET- blue, SET- yellow, and CET- green, respectively.
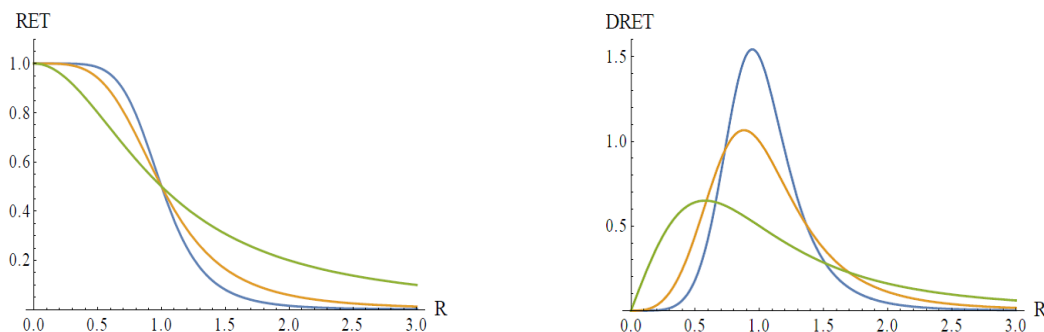
Figure 4. Behavior of the RET efficiency functions $E_i(d, x, \eta_i)$, and their derivation. $DE_i(d, x, \eta_i) = \partial E(d, x, \eta_i) / \partial d$ for FRET- blue, SET- yellow, and CET- green, respectively.

5. Unified RET theory

The normalized FRET rate k can be calculated by electric Green function method [4, 16]

$$k(R) = 18\pi\varepsilon_0^2 c^4 \int_0^\infty \frac{d\omega}{\omega^4} f_D(\omega) f_A(\omega) M(\omega), \tag{10}$$

where ω is the transfer frequency, c is the speed of light, ε_0 is the dielectric constant of the media $M_{(\omega,R)}$ is the Green function, $f_D(\omega)$ and $f_A(\omega)$ are the normalized transfer spectrum of D and A, respectively. Using a some kind of unified theory, we have [16, 17]

$$M(\omega) = \frac{1}{(4\pi\varepsilon_0)^2} K^2 G_A(\omega)^2 G_D(\omega)^2 \frac{1}{R^6} \left[3 + (\omega R/c)^2 + (\omega R/c)^4\right], \tag{11}$$

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). We note that in the equation (11) there are 3 terms with R^{-6}, R^{-4}, and R^{-2} dependence.

6. Simple model for nanoparticles concentration dependence of intensity

In this part, for explaining the observed unconventional with both fluorescence intensity enhancement and quenching depending on the concentration of GNPs, we propose a simple two branches surface plasmon polariton model.

We consider a two branch model of surface plasmon polariton for GNPs. Because the obsorption spectra of GNPs are quite broaded (see the figure 3), both two branches give their contribution to the energy transfer processes.

The Green fuction M can be written as

$$M(\omega, \langle R \rangle) = \frac{1}{(4\pi\varepsilon_0)^2} K^2 G_A(\omega)^2 G_D(\omega)^2 \left[\frac{3}{\langle R \rangle^6} + \frac{(\omega/c)^2}{\langle R \rangle^4} + \frac{(\omega/c)^4}{\langle R \rangle^2}\right], \tag{12}$$

where $\langle R \rangle$ is the average D-A distance. In the equation (12) just are 3 contributions given by FRET, SET, and CET-mechanisms respectively.

Based on that fact, we assume a GFRET model with mixing 3 mechanisms: FRET, SET, and CET-mechanisms. Considering a simple relation between the average donor-acceptor distance $\langle R \rangle$ and NPs concentration n as $\langle R \rangle \sim (n_A + n_D)^{1/3} \approx n^{-1/3}$ we have
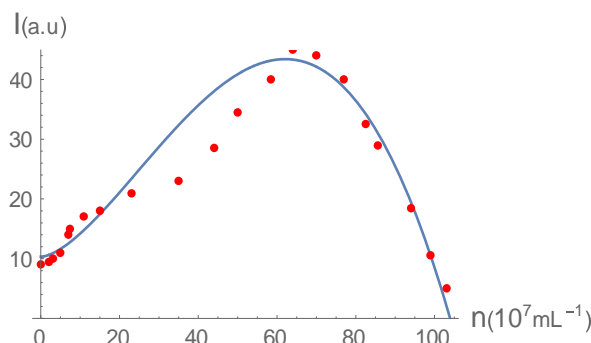
$$M(\omega, \langle R \rangle) = \frac{1}{(4\pi\varepsilon_0)^2} K^2 G_A(\omega)^2 G_D(\omega)^2 \left[An^2 + Bn^{4/3} + Cn^{2/3}\right], \tag{13}$$

where A, B, and C are some parameters.

Taking the ussual linear optic condition $(G_A G_D)^2 \sim n$, the normalized intensity I is

$$I_{(n)} = I_0 + an^3 + bn^{7/3} + cn^{5/3}, \tag{14}$$

where a, b, and c are the parameters, I_0 is the the normalized intensity at $n \approx 0$.

Figure 5. Theory-experimental comparison of unconventional fluorescence enhancement and quenching depending on the concentration of GNPs. The blue curve is obtained from equation (14) with the fitting parameters $a = -8.70925 \cdot 10^{-5}$, $b = -2.69385 \cdot 10^{-3}$, $c = 9.7635 \cdot 10^{-2}$, $I_o = 10.32$ the experiment data are in red cycles.

As an example we take the case of RET between OBs and GNPs (see the figure 3). In the figure 5 we present the curve (14) of OBs unconventional fluorescence enhancement and quenching depending on the concentration of GNPs with the fitting parameters $a = -8.70925.10^{-5}$, $b = -2.69385.10^{-3}$, $c = 9.7635.10^{-2}$, $I_o = 10.32$, also the experiment data in red cycles. We obtained the quite good agreement between the calculated values of normalized intensity from our model and experimental data.

7. Discussion

In this work concentration of GNPs dependence of energy transfer occurs between the fluorophores and GNPs is investigated. For explaining the observed unconventional with both fluorescence intensity enhancement and quenching depending on the concentration of GNPs, a simple two branches surface plasmon polariton model is proposed. Because the absorption spectra of GNPs are quite broad both two branches give their contribution to the energy transfer processes. The concentration depending is simple with 3 fitting parameters a, b, and c describing the FRET, SET and CET contributions, respectively.

As an example, we took the case of energy transfer between OBs and GNPs, and obtained quite good agreement of the theoretical results with experimental data. The sign of a and b are negative describe the quenching effect in conventional RET. While the sign of c is positive describes the enhancement by CET mechanism observed in unconventional RET experiments. Those signs are agreed with surface plasmon polarition picture.

Acknowledgments

References

[1]   Yun C S, Javier A, Jennings T, Fisher M, Hira S, Peterson S, Hopkins B, Reich N O, and Strouse G F 2005 Nanometal Surface Energy Transfer in Optical Rulers, Breaking the FRET Barrier *J. Am. Chem. Soc.* **127** 3115

[2]   Bhowmick S, Saini S, Shenoya V B, and Bagchi B 2006 Resonance energy transfer from a fluorescent dye to a metal nanoparticle *J. Chem. Phys.* **125** 181

[3]   Wong K F, Bagchi B, Rossky P J. 2004 Distance and orientation dependence of excitation transfer rates in conjugated systems: beyond the Forster theory *J. Phys. Chem. A* **108** 5752

[4]   Vincent R, Carminati R 2011 Magneto-optical control of Forsterr energy transfer *Phys. Rev. B* **83** 165

[5]   Gulin-Sarfraz T, Sarfraz J, Karaman D S, Zhang J, Oetken-Lindholm C, Duchanoy A 2014 FRET-reporter nanoparticles to monitor redox-induced intracellular delivery of active compounds *RSC Adv.* 4 16429

[6]   Yaghini E, Giuntini F, Eggleston I M, Suhling K, Seifalian A M, MacRobert A J. 2014 Fluorescence Lifetime Imaging and FRET-Induced Intracellular Redistribution of Tat Conjugated Quantum Dot Nanoparticles through Interaction with a Phthalocyanine Photosensitiser *Small.* **10** 782

[7]   Singh H, Bagchi B. 2005 Non-Forster distance and orientation dependence of energy transfer and applications of fluorescence resonance energy transfer to polymers and nanoparticles: How accurate is the spectroscopic ruler with 1/R6 rule?", *Curr. Sci.* **89** 1710

[8]   Jennings T L, Singh M P, Strouse G F. 2006 Fluorescent Lifetime Quenching near d = 1.5 nm Gold Nanoparticles: Probing NSET Validity *J. Am. Chem. Soc.* **128** 5462

[9]   Pons T, Medintz I L, Sapsford K E, Higashiya S, Grimes A F, English D S 2007 On the Quenching of Semiconductor Quantum Dot Photoluminescence by Proximal Gold Nanoparticles *Nano Lett.* **7** 3157

[10]   West R G, Sadeghi S M 2012 Enhancement of Energy Transfer between Quantum Dots: The Impact of Metallic Nanoparticle Sizes *J. Phys. Chem. C* **116** 20496

[11]   Zhang X, Marocico C A, Lunz M, Gerard V A, Gun'ko Y K, Lesnyak V 2012 Wavelength,

Concentration, and Distance Dependence of Nonradiative Energy Transfer to a Plane of Gold Nanoparticles *ACS Nano* **6** 9283

[12] Zhang X, Marocico C A, Lunz M, Gerard V A, Gun'ko Y K, Lesnyak V, Gaponik N, Susha A. S, Rogach A L, and Bradle A L 2014 Experimental and Theoretical Investigation of the Distance Dependence of Localized Surface Plasmon Coupled Forster Resonance Energy Transfer, *ACS Nano* **8** 1273

[13] Lunz M, Zhang X, Gerard V A, Gun'ko Y K, Lesnyak V, Gaponik N 2012 Eff ect of Metal Nanoparticle Concentration on Localized Surface Plasmon Mediated Forster Resonant Energy Transfer *J. Phys. Chem. C* **116** 26529

[14] Lakowicz J R 2005 Radiative decay engineering 5: metal-enhanced fluorescence and plasmon emission *Anal. Biochem.* **337** 171

[15] Breshike C J, Riskowski R A, and Strouse G F 2013 Leaving Forster 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** 23942

[16] Ha C V, Nga D T, Viet N A, Nhung T H 2015 The local field dependent eff ect of the critical distance of energy transfer between nanoparticles *J. Opt Comm* **353** 4955.

[17] Thien T V, Hoa N M, Quyen B T L, Xuan L V, Ha C V, Nga D T, Viet N A 2014 Forster resonance energy transfer (FRET) with a metal nanoparticle and surface plasmon energy transfer (SET) mechanism *Proc.8th Opt. Conf. (Danang) 472-477.*

[18] Andrews D L, Bradshaw D S 2004 Virtual photons, dipole fields and energy transfer: a quantum electrodynamical approach", *Eur. J. Phys.* **25** 845858