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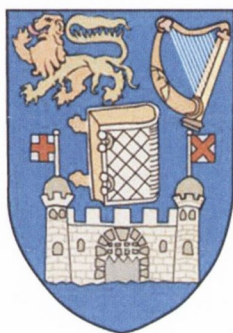
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Localised Surface Plasmon Mediated Energy Transfer in Quantum Dot Systems

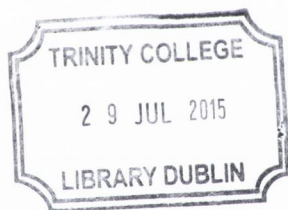


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Doctor of Philosophy

2015



Thesis 10599

Declaration

This thesis has not been submitted as an exercise for a degree at this or any other university. The work described in this thesis is entirely my own, with exception of assistance recognised in the acknowledgments and the collaborative work noted in the publications. I agree that Trinity College may lend or copy this thesis on request.

Xia Zhang
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XIA ZHANG
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List of Publications and Conference Contributions

List of Publications

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- Lunz, Manuela, **Xia, Zhang**, Valerie A. Gerard, Yurii K. Gun'ko, Vladimir Lesnyak, Nikolai Gaponik, Andrei S. Sussha, Andrey L. Rogach, and A. Louise Bradley. "Effect of Metal Nanoparticle Concentration on Localized Surface Plasmon Mediated Förster Resonant Energy Transfer." *The Journal of Physical Chemistry C* 2012, 50, 26529-26534.

- **Xia, Zhang**, Cristian A. Marocico, Manuela Lunz, Valerie A. Gerard, Yurii K. Gun'ko, Vladimir Lesnyak, Nikolai Gaponik, Andrei S. Sussha, Andrey L. Rogach, and A. Louise Bradley. "Experimental and Theoretical Investigation of the Distance Dependence of Localized Surface Plasmon Coupled Förster Resonance Energy Transfer." *ACS Nano* 2014, 2, 1273-1283.

- **Xia, Zhang**, Manuela Lunz, Valerie A. Gerard, Yurii K. Gun'ko, Vladimir Lesnyak, Nikolai Gaponik, and A. Louise Bradley. "Enhanced quantum efficiency in mixed donor-acceptor nanocrystal quantum dot monolayers." *2011 13th International Conference on Transparent Optical Networks (ICTON)*, IEEE, 2011, pp. 1-4.

- Lunz, Manuela, **Xia, Zhang**, Valerie A. Gerard, Yurii K. Gun'ko, Vladimir Lesnyak, Nikolai Gaponik, Andrei S. Sussha, Andrey L. Rogach, and A. Louise Bradley. "Modification of the FRET rate in quantum dot structures." *2011 13th International Conference on Transparent Optical Networks (ICTON)*, IEEE, 2011, pp. 1-4.

- **Xia, Zhang**, Valerie A. Gerard, Yurii K. Gun'ko, Vladimir Lesnyak, Nikolai Gaponik, Andrei S. Sussha, Andrey L. Rogach, and A. Louise Bradley. "Large energy transfer dis-

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Abstract

Nonradiative energy transfer to metal nanoparticles (NPs) is a technique used for optical-based distance measurements which is often implemented in sensing. Both Förster resonant energy transfer (FRET) and nanometal surface energy transfer (NSET) mechanisms have been proposed for emission quenching in proximity to metal NPs. Here quenching of emission of colloidal quantum dots (QD) in proximity to a monolayer of gold NPs is investigated. Five differently sized CdTe QDs are used to probe the wavelength dependence of the quenching mechanism as their emission peak moves from on resonance to off resonance with respect to the localized surface plasmon (LSP) peak of the Au NP layer. The Au NP concentration and distance dependences of energy transfer are discussed. Photoluminescence quenching and lifetime data are analyzed using both FRET and NSET models and the extracted characteristic distances are compared with theory. Good agreement with FRET theory has been found for QDs with emission close to the LSP resonance, though larger than expected Förster radii are observed for QDs with emission red-shifted with respect to the LSP peak. Closer agreement between experimental and theoretical characteristic distances can be found across the full wavelength range within a NSET approach.

The LSP coupled FRET is experimentally investigated using a trilayer structure composed of separated monolayers of donor and acceptor QDs with an intermediate Au NP layer. The dependence of the energy transfer efficiency, rate, and characteristic distance, as well as the enhancement of the acceptor emission, on the separations between the three constituent layers is examined. A d^{-4} dependence of the energy transfer rate is observed for LSP-coupled FRET between the donor and acceptor planes with the increased energy transfer range described by an enhanced Förster radius. The conventional FRET rate also follows a d^{-4} dependence in this geometry. The experimental data can be used to validate a theoretical model. Further theoretical study about the influence of the placement of the intermediate Au NP proves that donor-plasmon coupling has a greater influence than

acceptor-plasmon coupling on the characteristic energy transfer range in this LSP-coupled FRET system. The LSP-enhanced Förster radius is dependent on the intermediate Au NP concentration. The potential to tune the characteristic energy transfer distance through Au NP concentration has implications for applications in nanophotonic devices or sensors.

A new approach to enable quantum well (QW) pumping QDs through FRET, which is limited to the close proximity, over longer distances is proposed and realised. The coupling of the QW and Au NPs with varying Au NP concentration has been analysed. The emission and decay lifetime are quenched by Au NPs. However, a further emission and lifetime quenching are observed by the adding of the QD monolayer. It is found that energy transfer can occur even at a QW-QD distance of 20.2 nm. With the aid of LSP, a ~ 1.9 fold enhancement of Förster distance, R_0 , is obtained, which greatly breaks the distance limit of QW-QD FRET pair. It makes it possible for the QW pumping QDs through nonradiative energy transfer over larger distances. Furthermore, a ~ 1.47 fold QD emission enhancement is obtained, which may enable the applications in QW-QD based color converters or light emitting diodes overcoming design issues related to the limited energy transfer distances.

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Chapter 1

Motivation

Global warming has become an undisputed serious problem caused by human activity, in particular the burning of fossil fuels, together with deforestation [1, 2]. Average surface temperatures have risen globally by about 0.75 °C over the past century [3]. The released greenhouse gases [4] are responsible for weather and climate changes.

In order to keep pace with the increasing thirst for energy worldwide, strong remedial action is demanded, as soon as possible, to avoid dangerous levels of warming and give a more secure future to wildlife. A key strategy is to replace fossil fuels-currently the main energy source -with sustainable, safe, clean and green energy sources [5]. Solar energy or photovoltaics generates electricity by converting sunlight, the earth's most abundant source. The total worldwide solar cell production in 2009 was >10 gigawatts (GW), which is more than ten times the worldwide production in 2000, and the cost has been reduced to under \$5/watt [6]. Despite much progress, the increasing energy demand requires better device performance with high light-to-electricity conversion efficiency but with the low cost. Many efforts have been devoted to improve light-to-electricity efficiency, one of which is using solution-processed quantum dot (QD) photovoltaics due to the low cost, ease of processing, physical flexibility and large area coverage [7]. QDs provide the feasibility of harvesting sunlight over entire visible region and infrared spectral ranges [8], as well as boosting light harvesting efficiency through multiple exciton generation [9]. More importantly, QDs can be served as "antennae" to enable transfer of excitation energy to other species when they are proximally incorporated into the architecture [10, 11] *via* nonradiative energy transfer mechanism such as Förster resonance energy transfer (FRET). Recently the incorporation of QDs and FRET into the dye sensitized solar cells has been reported, where QDs can effectively transfer energy to the dye [11, 12]. This proposed new paths for performance

optimisation of the solar cell.

QDs, behaving as a FRET donor or acceptor, intrigue scientific researchers not only because of the important role in optoelectronic devices, such as energy harvesting structures [13, 14], light emitting devices [15–18], but also because of the wide applications as imaging probes [19, 20] and in sensors [21–23]. For device implementation, quantum wells (QW) pumping QDs through FRET paves the way for the potentially use of QDs of tunable wavelengths in a variety of state-of-art light-emitting technologies, such as electronic displays, solid-state lighting and electrically pumped nanoscale lasers [15, 24].

For imaging probes or nanosensors, FRET has a well-defined distance dependence but suffers a limited length scale of approximately 10 nm. FRET ranges can be optimised through the selection of the properties of the FRET donor-acceptor pair, such as a high donor quantum yield and optimal spectral overlap of donor emission and acceptor absorption [25]. Nanosensors based on the localised surface plasmon (LSP) induced quenching of fluorophores continue to attract a lot of interest [26–28]. In particular the distance dependence of the quenching process of molecular dyes [29] and colloidal QDs [26, 30] by Au nanoparticles (NPs) created the basis for a plasmon-ruler [31] with an extended range compared to the previously proposed nano-ruler based on FRET between two fluorescent molecules [25, 32]. To date, most of the research concentrate on developing the method to link the QD and Au NPs for biosensing applications [33–43]. Quite limited investigations exist on the probing the nature of the energy transfer [30]. Furthermore, it is still unclear whether the energy transfer mechanism behind the quenching effect of the Au NPs is FRET or nanometal surface energy transfer (NSET). FRET efficiency for a single donor-acceptor pair follows a d^{-6} distance dependence [25] while NSET efficiency follows a d^{-4} distance dependence [31]. The distance dependent quenching effect by Au NPs can be described by FRET theory in Ref. [37, 44–48] but by NSET theory in Ref. [29–31, 49, 50]. It raises a question that what is the nature behind the "inconsistent" distance dependent energy transfer to the Au NPs, even with the comparable diameter? What parameters will have an impact on the distance dependence? A good understanding of the distance dependence is important for the design of nanosensors.

Apart from the route towards longer range of energy transfer *via* efficient quenching by metal NPs [31, 51], plasmonic structures provide an other route *via* LSP coupled FRET. LSP coupled FRET between donor-acceptor pairs has been theoretically investigated [52–54]. Experiments have verified that the enhancement of the energy transfer rate, efficiency, and

range is achieved in different geometries with a variety of emitters and metal NPs [51, 55–65]. However, LSP coupled FRET can be inhibited or even switched off [66, 67]. Increases in the energy transfer rate, efficiency and range can be expected depending on the plasmonic properties of the metal NP, and the relative positions of the donor and acceptor. With three constituent elements (namely donor, acceptor and plasmonic structure), LSP coupled FRET is a complex mechanism with a large number of parameters that can be dependent. The near-field of plasmonic nanostructures modifies the emission of the donor and acceptor and influences their near-field interaction through LSP coupled FRET. The FRET mechanism between the donor and acceptor competes with other decay mechanisms. Therefore, the various dependences need to be fully investigated and well understood to develop systems which can take advantage of plasmon controlled FRET for light emission, light harvesting or sensing applications.

In brief, the main aim of this thesis is to probe the nature of LSP induced quenching of QDs as well as study various dependences of LSP coupled energy transfer. Colloidal CdTe QDs of various emission wavelengths are selected to pair with colloidal Au NPs through layer-by-layer assembly. Layer-by-layer [68–70] is a versatile bottom-up nanofabrication technique, which can be used to fabricate QD or Au NP film with a controllable layer separation of nanometer-scale precision. Furthermore, it enables the controllable NP concentration in the layer, which facilitates us to investigate both the distance and Au NP concentration dependences. Not only limited to the probing the mechanism as discussed above, we will apply the idea of the LSP coupled FRET on quantum well-QD system, which has potential applications in colour converters [24, 71], light emitting diodes [72], and white light generation [18, 73]. Achermann *et al.* experimentally developed the approach of efficient pumping *via* nonradiative energy transfer from InGaN/GaN QW to the proximal QDs layer [15, 24]. However, the proximal separation is a prerequisite in practical implementation to enable efficient pumping. For the purpose of high FRET efficiency, many efforts have been devoted to the optimization of architectures [74, 75] to obtained optimal interaction volume or QW deposited with graded QDs [74] to enable efficient energy transfer. We will propose a new approach based on the idea of the LSP coupled FRET to enable QW pumping QDs with high efficiency and over long distances.

Therefore, in this thesis, **Chapter 2** will introduce some general optical properties of QDs, their advantages over molecular fluorophores as well as their potential applications. The basics of the LSP and the effect on the emission of the emitters are concisely introduced. The main experimental reports as well as theoretical explanations of the quenching by Au

NPs are given. In the end, the experimental and theoretical reports on the LSP coupled FRET and QW pumping QDs are presented briefly.

All the details about the sample preparation and characterisation techniques can be found in **Chapter 3**. It includes how we control the layer separation and NP concentration, how we calculate the concentration of QD and Au NPs, quantum yield of QDs, how we measure our samples and how we use the experimental data to probe the energy transfer mechanism.

In **Chapter 4**, in order to probe the nature of the quenching effect by Au NPs, five differently sized CdTe QDs are used to study the wavelength dependence of the quenching mechanism as their emission peak moves from on resonance to off resonance with respect to the LSP absorption peak of the Au NP layer. Apart from the donor emission wavelengths, both of the distance and Au NP concentration are also tuned to probe the dependences. To the best of our knowledge this is the first study of the QD-Au NP energy transfer mechanism as a function of the QD-Au NP separation, donor emission wavelength as well as Au NP concentration in a planar geometry. The Au NP concentration and distance dependences of energy transfer are analysed and compared with FRET and NSET theories in detail.

The distance and Au NP concentration dependences of LSP coupled FRET are examined using a trilayer structure comprised of separated monolayers of donor and acceptor QDs with an intermediate Au NP layer in **Chapter 5**. The dependences of the energy transfer efficiency, rate and characteristic distance, as well as the enhancement of the acceptor emission, on the separations between the three constituent layers is presented. The experimental data is used to validate a theoretical model, which is used to give more insight into LSP mediated FRET.

LSP coupled energy transfer between a QW and QDs is investigated in **Chapter 6**. The characterisation of the QW-only, the emission and lifetime quenching of QW by Au NPs in QW-Au NP structures are reported. Finally, QW-Au NP-QD structures are prepared to study the LSP effect on the FRET between QW and QDs over larger separations.

Conclusions are presented in **Chapter 7**, with some comments on the future study.

Chapter 2

Background

2.1 Semiconductor Quantum Dots

"There's Plenty of Room at the Bottom", the famous talk given by Richard Feynman in 1959 [76], depicts a new world of "Nano" Nanoscience and nanotechnology emerged and have exploded in the last 50 years. This branch of science explores the world, manipulates and controls matter at the atomic scales [77]. Due to the reduced size on the nanoscale (1-100 nm) in at least one dimension of nanomaterials, the physical and chemical properties can differ significantly from those of the atomic, molecular or bulk materials of the same composition [78]. Based on the number of dimensions confined on the nanoscale, nanomaterials can be classified [79] into *0D nanomaterials*, materials with three dimensions in nanoscale are typically nanoparticles (NPs). *1D nanomaterials*, materials with two dimension in nanoscale are typically nanowires, nanorods, nanotubes. *2D nanomaterials*, materials with one dimensions in nanoscale, such as thin films or surface coatings. Of particular interest is 0D quantum dot (QD) with unique properties, which paves the way towards new generation devices applications.

2.1.1 Fundamentals

QDs, or semiconductor nanocrystals (NCs), are quasi-zero dimension objects, which were discovered by the Brus group [80, 81] in 1983. A colloidal QD comprises of 10^2 - 10^4 atoms with the shape of hexagonal prism or tetrahedron [82, 83], which is roughly spherical in shape. The size of a QD typically ranges 1-10 nm in diameter[83]. A schematic as well as electron microscope image of QDs are shown in Fig 2.1.

Distinct from either molecules or bulk materials, QDs in general have a strong tendency

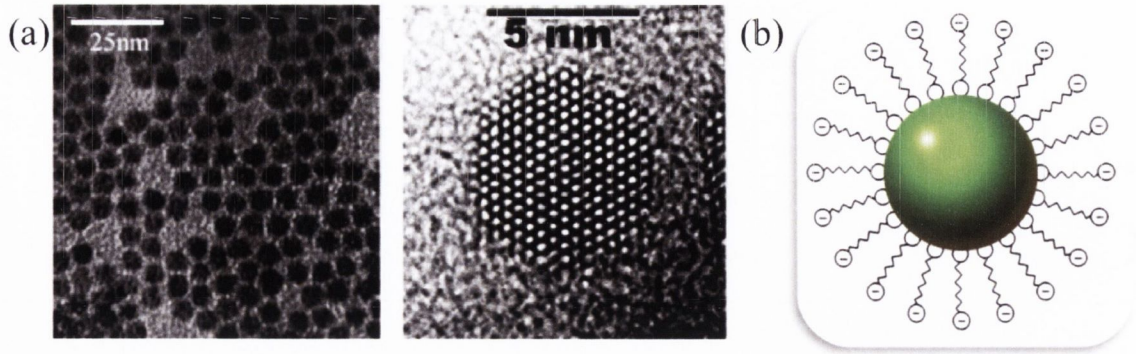


Fig. 2.1 (a) TEM image of CdSe QDs with scale bar of 5 nm. The image is taken from Ref. [91]. (b) Schematic graph of a core-only QD with capping ligands. A single QD is commonly approximated as a sphere.

to aggregate owing to the presence of a large number of highly active surface atoms. Stabilization of QDs is necessary for both exploring their intrinsic properties and enabling their technical applicability [84]. The inorganic core, consisting of the semiconductor material, is capped by an organic outer layer of surfactant molecules (“ligands”), which provide sufficient repulsion to prevent them from aggregating [85] as well as oxidizing, and provides stabilization the NPs in the solution. Nevertheless, this passivated “core-only” type QDs typically exhibit low quantum yield (QY) due to surface related trap states acting as fast non-radiative de-excitation channels for photogenerated charge carriers [84, 86]. QY, denoted as Φ , is defined as the ratio of the number of emitted photons to the number of absorbed photons, which can also be described in terms of radiative decay rate k_r and nonradiative decay rate k_{nr} as in eq 2.1.

$$\Phi = \frac{k_r}{k_r + k_{nr}} \quad (2.1)$$

One important strategy is the overgrowth of the QD core with a shell of a second semiconductor, resulting in a core-shell type QDs [84]. The shell reduces the surface defects and the blinking [87–89], the fluctuation of “on” and “off” states in a single QD. Core-only type CdTe QDs are used in this thesis, with the QYs up to 50%. However, the QYs of core-only CdTe QDs can go up to 80% through the state-of-art synthesis [90].

2.1.2 Size Dependent Optical Properties

As the QD diameter is reduced below the effective exciton Bohr exciton radius [92], quantum confinement [93, 94] results in an increase of the bandgap energy, E_g^{QD} , which can be

estimated simply according to the equation [95] eq 2.2 as

$$E_g^{QD} = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2r^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - 1.786 \frac{e^2}{\epsilon r} - 0.248 E_{Ry}^* \quad (2.2)$$

where the first term E_g^{bulk} is the bandgap energy of the bulk solid; the second term is the exciton energy which behaves as a "particle-in-a-box"; the third term is electron-hole coulomb attraction. r is radius of the QD, m_e , m_h are the effective mass of the electrons and holes, ϵ is the dielectric constant of the semiconductor [96]. E_{Ry}^* is the Rydberg energy for the electron-hole pair, which is generally small compared to the second term, the latter dominating the energy change with a strong dependence on size [95]. The band gap increases with decreasing the radius of the QD. Correspondingly, the physical properties, in particular the optical ones, are strongly size dependent. Spectral tunability facilitates absorption and emission wavelengths ranging across the visible range, shown in Fig 2.2.

Fig 2.2 shows the absorption and photoluminescence (PL) spectra of QD solution. The QD emission spectrum is symmetric and Gaussian-like; full width of half maximum (FWHM) ranges from 25-35 nm [97]. The emission profile of perfect QDs ensemble, with exactly N atoms per QD, should be quite narrow. However, there are always $(N \pm \Delta N)$ atoms per QD, namely a finite size distribution in real ensembles, resulting in inhomogeneous energy broadening. The samples whose deviation from the mean size is less than or equal to 5-10% are termed as "monodisperse" QDs [98]. Furthermore, there is an energy difference of the emission energy with respect to 1st absorption band energy, referred to as "Stokes shift".

2.1.3 Quantum Dot Advantages Over Molecular Fluorophores

QDs overcome limitations of molecular fluorophores in many aspects, such as their narrow and tunable emission lines, higher photostability and high quantum yields [99, 100]. The broad absorption of QDs enables free selection of the excitation wavelength and thus straightforward separation of excitation and emission [100]. A single power source can be used to excite QDs with different emission wavelengths. However, multiple excitation sources are needed to excite different fluorescent dyes efficiently due to their narrow absorption band [95]. Furthermore, QDs dispersed in solution have a high quantum yield [101–104], which have enhanced photostability and superior resistance to photo-bleaching [102]. These advantages facilitate increasing the signal-to-noise by increasing the excitation rate and enable application in single-molecule spectroscopy experiments [105].

Due to their advantages, QDs have gained a lot of popularity as imaging probes [19, 20]

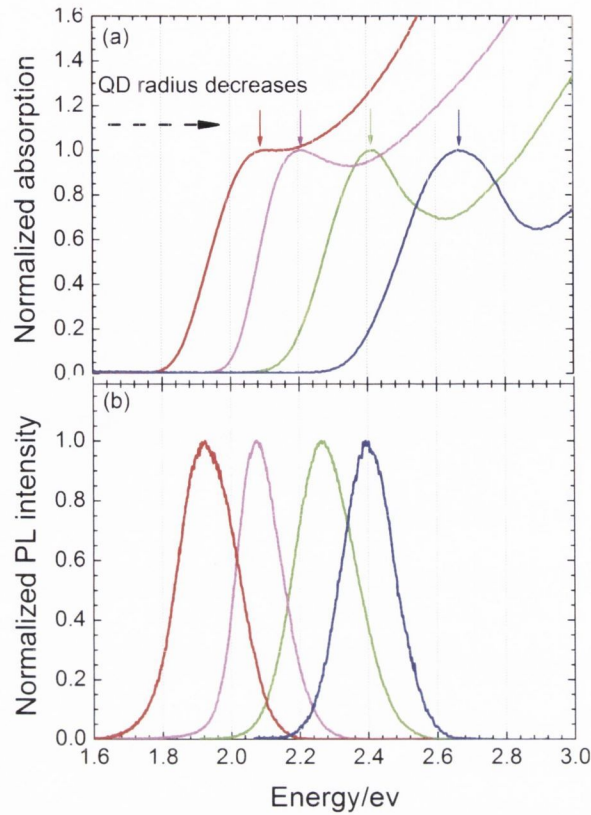


Fig. 2.2 (a) Absorption spectra of the core-only CdTe QDs dispersed in water. The corresponding $1S_e$ - $1S_h$ absorption peaks are shown. (b) The normalised photoluminescence spectra of the same QDs as shown in (a) at the excitation wavelength of 400 nm measured at room temperature. The energy difference of absorption and emission peak is the "Stokes shift".

and also devices such as photovoltaic cells [10], photodetectors [8], sensors [21–23], energy harvesting structures [13, 14], and light emitting devices [15–18].

2.2 Förster Resonance Energy Transfer

2.2.1 FRET Theory

Förster Resonance Energy Transfer (FRET), named after scientist Theodor Förster [25, 106], is a nonradiative energy transfer process mediated by near field dipole-dipole interaction. As shown in Fig 2.3 for a single pair of donor-acceptor QDs, the donor is excited by a light source [107], which has more energy than the bandgap energy. It subsequently vibrationally relaxes to the lowest excited electronic states very fast ($< \text{or} = 1 \text{ ps}$) [108–110]. In the absence of an acceptor, the donor relaxes to its ground state by emitting a photon *via*

radiative recombination across $1S_e-1S_h$ with the rate k_r and nonradiative recombination with the rate k_{nr} , where $k_r + k_{nr} = \tau_D^{-1} = k_D$, τ_D is the intrinsic decay lifetime of donor without acceptor while k_D is the corresponding donor decay rate. If there are available acceptor electronic states with resonant energy levels with the donor states $1S_e-1S_h$ and at proximal distance of the donor, energy transfer from donor to acceptor over time scales of nanoseconds. The acceptor relaxes very fast vibrational relaxation which prevents back transfer to donor and finally the excitation decays radiatively or nonradiatively.

The signatures of FRET are donor emission quenching, donor lifetime quenching, acceptor emission enhancement and acceptor decay lifetime increase. Ideally, the acceptor is not excited and any acceptor emission is indication of energy transfer. However, in most cases, the acceptor and donor are both excited by the light source. For the donor-only and acceptor-only systems, the excited-state population after the light excitation can be described by $\frac{dD(t)}{dt} = -k_D D(t)$, $\frac{dA(t)}{dt} = -k_A A(t)$, where $D(t)$, $A(t)$ are the concentration of the donor, acceptor QDs in the excited states. k_A is the acceptor decay rate. In the donor-acceptor systems in the presence of FRET, the excited-state population can be described by [111]

$$\begin{aligned}\frac{dD(t)}{dt} &= -(k_D + k_t)D(t) \\ \frac{dA(t)}{dt} &= D(t)k_t - k_A A(t)\end{aligned}\tag{2.3}$$

FRET adds a new decay channel to the donor while acceptor has an additional pumping from the donor with the energy transfer rate k_t . Solving the above equations, it yields,

$$D(t) = D_0 e^{-(k_D + k_t)t}\tag{2.4}$$

$$A(t) = -\frac{D_0 k_t}{k_D + k_t - k_A} e^{-(k_D + k_t)t} + \frac{D_0 k_t}{k_D + k_t - k_A} e^{-k_A t}\tag{2.5}$$

where D_0 is the excited state population at $t = 0$. The incorporation of the term k_t in the eq 2.4 indicates that FRET results in the shortening of the donor decay lifetime. The negative term in the eq 2.5 reflects a rise component due to the energy transfer from the donor to acceptor with rate constant $(k_D + k_t)$ [95, 111]. Franzl *et al.* reported that the acceptor decay lifetime increases from 164 ps for the acceptor monolayer to 215 ps for the donor-acceptor bilayer CdTe QDs because the acceptor are fed by donor *via* FRET [112]. Nizamoglu *et al.* reported that the acceptor QDs decay lifetime increases from 17.66 ns to 22.59 ns due to energy transfer in the mixed size QDs [113].

Besides the spin-singlet energy transfer shown in Fig 2.3, it has been reported that the trapped excitons by defect states or spin-triplet excitons can also involve in FRET process, both of which can contribute to the emission enhancement and rise-time increase in acceptor species [13, 114]. Therefore, we used emission or lifetime quenching of the donor rather than emission or lifetime increase to characterise FRET efficiency in this thesis.

The rate of dipole-dipole resonance energy transfer, k_{FRET} , between a donor and an acceptor separated by a fixed distance, d , was shown to be [115]

$$k_{\text{FRET}} = \frac{1}{\tau_D} \cdot \left(\frac{R_0}{d} \right)^6 \quad (2.6)$$

The FRET efficiency is then

$$\begin{aligned} E_{\text{FRET}} &= \frac{k_{\text{FRET}}}{k_{\text{FRET}} + \tau_D^{-1}} \\ &= \frac{1}{1 + (d/R_0)^6} \end{aligned} \quad (2.7)$$

where R_0 is termed as the Förster distance, which is the donor-acceptor separation at which the intrinsic rate equals the energy transfer rate or where energy transfer efficient is 50% (see Fig 2.4). It can be seen that E_{FRET} is sensitively dependent on the donor-acceptor d or d/R_0 and therefore, FRET is widely used to elucidate distances between biomolecules, termed as a “spectroscopic ruler” [32, 97].

Eq 2.6 and eq 2.7 are only applicable for a single donor-acceptor pair. If a donor is interacting with multiple acceptors, the energy transfer rate k_{FRET} is the sum of each energy transfer rate, k_i , as

$$k_{\text{FRET}} = \sum_i k_i = \frac{1}{\tau_D} \sum_i \left(\frac{R_0}{d_i} \right)^6 \quad (2.8)$$

The energy transfer efficiency becomes

$$\begin{aligned} E_{\text{FRET}} &= \frac{k_{\text{FRET}}}{k_{\text{FRET}} + \tau_D^{-1}} \\ &= \frac{1}{1 + [\sum_i (\frac{d_i}{R_0})^6]^{-1}} \end{aligned} \quad (2.9)$$

R_0 can be used to compare FRET ranges for various donor-acceptor pairs. It is determined

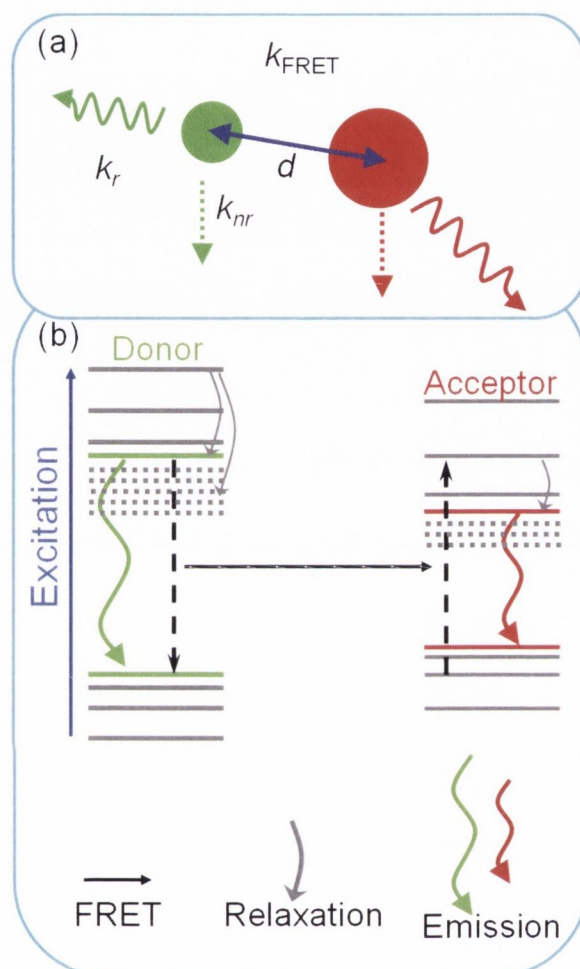


Fig. 2.3 Schematic depicting (a) FRET process between a smaller QD with higher energy bandgap (green) and a larger QD with smaller energy bandgap (red). The distance between the donor and acceptor is the centre-to-centre separation. (b) Simplified energy level diagram of two different sized QDs illustrating the basic FRET principle. Under excitation, the donor is excited from electronic ground state to an excited state, which is followed by very fast relaxation to the lowest excited states from where finally decay radiatively with the rate k_r or decay nonradiatively with the rate k_{nr} . If there is an acceptor with resonant energy states in close proximity, the transfer mechanism leads to an electronic transition from a lower to a higher energy level in acceptor. The energy transfer rate is k_{FRET} . Very fast relaxation in the acceptor to the lowest excited states prevents the back energy transfer to the donor. The acceptor finally decays radiatively or nonradiatively by relaxing to its ground state.

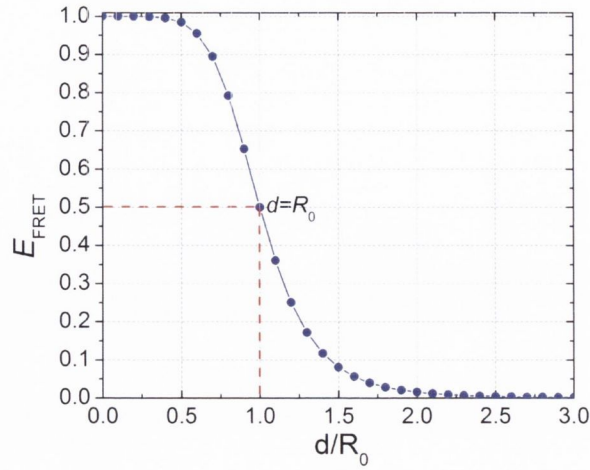


Fig. 2.4 Energy transfer efficiency between a single donor-acceptor pair E_{FRET} as a function of d/R_0 based on eq 2.7.

by the physical properties of the donor-acceptor pair and described by,

$$R_0 = 0.0211 \left[\frac{\kappa^2 \Phi_D J(\lambda)}{n^4} \right]^{\frac{1}{6}} \quad (2.10)$$

which yields R_0 in units of nm where n is the refractive index, κ^2 is dipole orientation factor between the donor and acceptor, Φ_D is the emission quantum yield of the donor in absence of the acceptor and $J(\lambda)$ is the spectral overlap of the area-normalised donor QD emission spectrum $\hat{f}_D(\lambda)$ and acceptor extinction spectra, $\epsilon_{\text{Acc}}(\lambda)$, which is expressed by

$$J = \int_0^\infty \hat{f}_D(\lambda) \cdot \epsilon_{\text{Acc}}(\lambda) \cdot \lambda^4 d\lambda \quad (2.11)$$

with

$$\hat{f}_D(\lambda) = \frac{F_D(\lambda)}{\int F_D(\lambda) d\lambda} \quad (2.12)$$

where $\hat{f}_D(\lambda)$ is the donor emission per unit wavelength integrated over the donor emission spectrum $F_D(\lambda)$, in units of nm^{-1} . The extinction spectrum of acceptor ϵ_{Acc} is in units of $\text{M}^{-1}\text{cm}^{-1}$ while J is in units of $\text{nm}^4\text{M}^{-1}\text{cm}^{-1}$.

The orientation factor is the square of κ , κ is given by

$$\kappa = \hat{d} \cdot \hat{a} - 3(\hat{d} \cdot \hat{r})(\hat{r} \cdot \hat{a}) \quad (2.13)$$

where $\hat{d}$, $\hat{a}$ are the vector along donor and acceptor dipole respectively. $\hat{r}$ is the vector along donor-acceptor direction. The detailed discussion of κ^2 can be found in Ref. [106]. $\kappa^2 = 2/3$

for isotropic system, which is the case for all samples studied in this thesis.

2.2.2 FRET Characterisation

As mentioned earlier, for a donor-only system the QD has a decay lifetime, τ_D , determined by its radiative recombination rate, k_r , and the nonradiative recombination rate, k_{nr} [106]

$$\tau_D = \frac{1}{k_r + k_{nr}} \quad (2.14)$$

The quantum yield of donor-only, Φ_D , is determined by

$$\Phi_D = \tau_D \cdot k_r = \frac{k_r}{k_r + k_{nr}} \quad (2.15)$$

If there are acceptors in proximity, the donor decay lifetime becomes

$$\tau_{DA} = \frac{1}{k_r + k_{nr} + k_{\text{FRET}}} \quad (2.16)$$

The quantum yield of the donor with presence of an acceptor, Φ_{DA} , is

$$\Phi_{DA} = \tau_{DA} \cdot k_r = \frac{k_r}{k_r + k_{nr} + k_{\text{FRET}}} \quad (2.17)$$

Therefore, the FRET efficiency can be characterised as [116]

$$\begin{aligned} E &= \frac{k_{\text{FRET}}}{k_{\text{FRET}} + k_r + k_{nr}} \\ &= 1 - \frac{\Phi_{DA}}{\Phi_D} \\ &= 1 - \frac{\tau_{DA}}{\tau_D} \\ &= 1 - \frac{I_{DA}}{I_D} \end{aligned} \quad (2.18)$$

where I_{DA} and I_D are integrated emission intensities of the donor in the presence and absence of acceptor respectively. τ_D and τ_{DA} are experimentally measured decay lifetime of donor-only and donor with acceptor systems, respectively. Apart from the signatures of reduction in donor emission intensity and decay lifetime in FRET process, an emitting acceptor will have emission enhancement as well as an increase of rise-time of the time dependent acceptor emission, the details can be found in Ref. [116].

2.2.3 Distinguishing Other Excited Energy Transfer Mechanism

FRET efficiency can be characterised as discussed above, however, it is not always straightforward to establish whether the emission quenching of the donor, or the energy transfer mechanism, is FRET or due to other mechanisms, such as Dexter transfer [117], charge transfer.

When the donor is excited, energy transfer from donor to acceptor can occur *via* radiative and/or nonradiative routes. Nonradiative energy transfer is a one-step process as



where D^* , A^* denotes as the excited state of donor, acceptor while D , A denotes as the ground state of donor and acceptor respectively.

In contrast in a radiative process [118], an emitted photon from a donor is reabsorbed by an acceptor. It has a relatively long range, falling as $\frac{1}{r^2}$ [119] as



which is a two-step process with a real photon mediating the energy transfer.

Dexter transfer is a nonradiative process which occurs as a result of an electron exchange mechanism, which requires an overlap of the wavefunctions of the energy donor and energy acceptor [120]. The Dexter transfer rate k_{DET} decreases exponentially with the distance d , with a range of ~ 1 nm [121] as

$$k_{\text{DET}} = K \cdot J_{DT} \cdot e^{[-2d/L]} \quad (2.21)$$

where K is a constant related to specific orbital interactions. J_{DT} is the spectral overlap integral, which is similar to the spectral overlap J in FRET (eq 2.11) but does not depend on the acceptor extinction coefficient, and L is the sum of their van der Waals radii. Similar to Dexter transfer, charge transfer rate k_{CET} also decrease exponentially with distance d as

$$k_{\text{CET}} = K_0 \cdot e^{[-\beta d]} \quad (2.22)$$

but the energy transfer range can be ~ 2 nm. β characterise the energy transfer and K_0 is a preexponential factor. The details can be found in Ref. [122].

In the QDs system studied in this thesis, the centre-to-centre distance between donor

QD and acceptor QD is much larger than 2 nm, which is much larger than Dexter transfer range 1 nm, thus Dexter transfer can be excluded. As mentioned earlier, FRET is a process mediated by nonradiative dipole-dipole interaction with a length scale of ~ 10 nm [31], with a d^{-6} distance dependence. FRET breaks down for $d < 1$ nm due to ideal dipole approximation assuming that the dipole-dipole separation is much larger than the dipole itself. However, both emission and lifetime quenching involve in the FRET and charge transfer mechanism, it is impossible to establish the energy transfer mechanism is FRET or charge transfer from the quenching experimentally. As FRET depends on spectral overlap while charge transfer does not, and they have various distance dependences, tracking the energy transfer efficiency dependence through monitoring the spectral overlap or distance can provide further evidence to establish the mechanism.

2.2.4 FRET Reports in Quantum Dot Systems

QDs structures in 2D or 3D geometries can be prepared through top-down approaches, such as lithography [123] and molecular-beam epitaxy [102]; or bottom-up methods, namely chemical methods, such as Layer-by-Layer assembly [91, 124] and Langmuir-Blodgett [125], which facilitate the investigation of QD-QD coupling in close proximity.

FRET can not happen in diluted solutions as the QDs are sufficiently far apart as single QD but can occur in densely packed layers of QDs meeting the requirement of close donor-acceptor proximity. Kagan *et al.* [124, 126] firstly reported energy transfer in CdSe core-only QDs of different sizes with evidence of energy transfer from smaller to larger QDs. Crooker *et al.* [98] studied the energy transfer mechanism by time-resolved and spectrally-resolved photoluminescence, revealing that FRET could be optimized *via* QD size selection arranging an energy gradient. Beyond energy transfer in QDs with large size disparity, energy transfer is also observed in monodispersed QD due to the size distribution within ensemble [127]. Furthermore, the sequential stacking of green, yellow, orange and red emitting QDs builds an energy gradient, facilitated efficient directional FRET. Such “nanorainbow” [128] structure yields ~ 28 times emission enhancement, which is much higher than expected from FRET alone due to contributions from exciton recycling [13, 129]. In this case the exciton captured by defect states in the smaller QD transferred to bright states in larger QD.

It is intriguing whether or not a QD can be treated as a point dipole. A typical molecular chromophore is only about 1 nm while QDs are much larger than molecules, typically ranging in diameter from 2 to 8 nm [130], which is comparable to donor-acceptor distance

in FRET experiments. FRET formalism breaks down for molecular fluorophores as donor-acceptor pair. It raises a question of applicability of FRET theory in QD systems which deals with interaction between two point dipoles because FRET breaks down observed in molecules if the distance is comparable with the size [95]. However, theoretical studies [131, 132] have probed the validity of FRET in QD system and demonstrated that the interaction between QDs can be well described by FRET. The QD behaves as a potential formed by a positive charge and a negative charge separated by ~ 0.7 nm that are localised at the center of the QD [132], confirming the approximation of an QD as a point dipole.

The FRET formalism has been validated in QD-QD [13, 98, 133] systems as well as on QDs incorporated with other materials, such as QD-dye [99, 134], QD-protein [135], QD-graphene [136], and QD-semiconductor QW [15] paired systems.

The distance dependence varies for different geometries, such as a donor dipole paired with different acceptor dipole geometries, such as d^{-6} for acceptor point dipole, d^{-5} for acceptor quantum wire, d^{-4} for acceptor quantum well or dipole plane, which has been recently reviewed in Ref. [137].

2.3 Localised Surface Plasmon Resonance

As mentioned earlier, Förster resonance energy transfer (FRET) is a well-defined distance dependent dipole-dipole interaction [138, 139]. It has been widely used for measuring the distance between two fluorophores [32, 140]. However, as a spectroscopic ruler conventional FRET suffers from a limited length scale of approximately ~ 10 nm. To overcome the limitation of the FRET range between two fluorescent molecules [32, 138], Au NPs have been reported as an efficient non-fluorescent acceptor due to the localized surface plasmon resonance (LSPR) in visible ranges. The near-field of the plasmonic structure can modify the emission of an emitter [62, 141–143]. Depending on the plasmonic properties of the metallic NP and the separation, it can lead to quenching or enhancement of the emission [144, 145]. The modified emission can be a consequence of many processes such as non-radiative energy transfer to the metal NP, scattering and absorption by the metal NP, and changes in the emitter's radiative and nonradiative decay rates. The plasmonic NP can also modify the excitation rate.

LSPR are non-propagating excitations of the conduction electrons of metallic NPs coupled to the electromagnetic field as shown in Fig 2.5. Light induces a coherent oscillation of electrons between opposite surfaces of a NP. Au NPs with a diameter of 5-50 nm own LSPR at approximately ~ 520 -530 nm and have the ability to influence electronic transitions of a

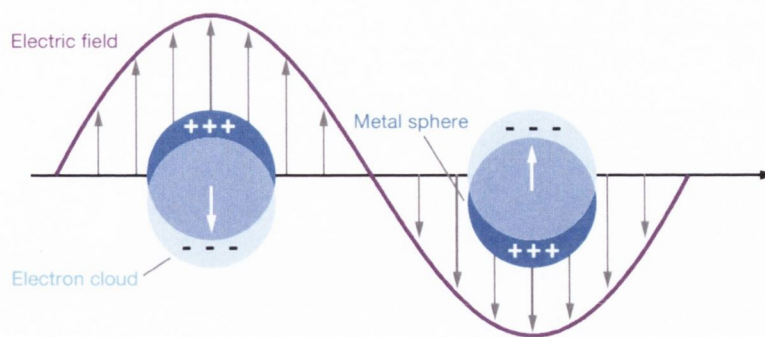


Fig. 2.5 Schematic of the LSPR reprinted from Willets *et al.* [148].

luminescent molecule in absorption and the emission channel. Furthermore, the molar extinction coefficient is several orders magnitude larger than that of molecular chromophores or QDs [95]. This enables Au NPs with diameter $d < 40$ nm and of distance > 2 nm to act as effective quenchers [146, 147]. Such energy transfer is promoted by the strong optical absorption inherent in plasmonic structures, which suggests that QDs and Au NPs could be excellent energy transfer donor-acceptor pairs.

2.3.1 Localised Surface Plasmon Induced Quenching Reports

The quenching effect by the Au NPs have been widely studied where Au NPs, behaving as the efficient energy acceptors, can pair with the donor organic dyes [29, 31, 49, 50, 143, 149, 150], the donor QDs [30, 37, 46–48] or fluorescent proteins [151]. The distance dependent quenching in single fluorophore-metal NPs pairs has been studied using variable length polypeptide [30] and DNA strands [29, 152], and more recently Au NPs incorporated in DNA origami [50]. The impact of the spectral overlap of the LSP resonance and the emission spectrum of the fluorophore on the quenching efficiency by the metal NP has been analyzed by varying the molecular dye or QD emission or the Au NP size [26, 147, 150]. In addition to the distance dependence of the QD emission quenching by near-by metal NPs [26, 30], the formation of oppositely charged QD-metal NP nano-assemblies in solution has been investigated and the observed QD emission quenching as a function of the QD-metal NP ratio was explained by energy transfer in predominantly single QD-single metal NP structures [40]. The dependence of the QD emission quenching efficiency on the spectral overlap with respect to the LSP resonance and the metal NP concentration are important characteristics for optimization of QD-metal based nanosensors and other photonic devices [153, 154].

2.3.2 Theoretical Explanation of the Quenching

Different analytical expressions have been used to describe the distance dependent energy transfer to the metal NP [29, 31, 37, 155, 156] and a general model does not exist yet. However, the generalization form can be expressed as

$$k_{ET} = \tau_D^{-1} \left(\frac{d_0}{d} \right)^n \quad (2.23)$$

where τ_D is the decay lifetime of the donor in the absence of the Au NP, d is the separation of the Au NP and the donor. d_0 is the characteristic distance with energy transfer efficiency of 50%. The formalism presented in Ref. [156] corresponds to $n = 6$ when d is larger than the radius of the Au NP and the donor, which is equivalent to FRET formalism as in Ref. [37].

The dipole-to-metal-particle energy transfer (DMPET) formalism in Ref. [155] takes into account the distance dependence of radiative and nonradiative decay rates, which is an extension of the FRET formalism. The DMPET efficiency for a single donor-acceptor pair can be described as

$$E_{DMPET} = \frac{1}{1 + \left(\frac{d}{R_0} \right)^6 \left[1 + \frac{1}{6} (2\pi n \cdot d / \lambda_{QD})^2 + \frac{1}{6} (2\pi n \cdot d / \lambda_{QD})^4 \right]^{-1}} \quad (2.24)$$

where the d is distance of the QD and Au NP, λ_{QD} is the emission wavelength of the QD. The DMPET efficiency depends on $(d/\lambda)^2$ and $(d/\lambda)^4$. In the system investigated in this thesis, λ_{QD} ranges ~ 500 - 700 nm while d ranges ~ 3 - 20 nm. At the short distances, DMPET efficiency follows a d^{-6} distance dependence similarly as FRET formalism, $E_{DMPET} = \frac{1}{1 + \left(\frac{d}{R_0} \right)^6}$ [30].

The NSET model in Ref. [29, 31] is an extension of the model in Ref. [157]. Persson [157] proposed that the damping rate of an oscillating dipole, which behaves as a donor, by a noble metal *surface*, which behaves as an acceptor, can be expressed as

$$k_{ET} = 0.3 \frac{\mu^2}{\hbar} \frac{\omega_D}{\omega_F k_F d^4} \quad (2.25)$$

where $\omega_F = 8.4 \times 10^{15}$ rad/s and $k_F = 1.2 \times 10^8$ cm $^{-1}$ are the bulk Au angular frequency and Fermi vector, respectively. μ is the dipole moment, d is the distance from the dipole to the Au sphere surface. Strouse and co-workers derived the NSET rate in a more measurable manner through including Einstein A_{21} coefficient [157], $A_{21} = \frac{\omega_D^3}{3\epsilon_0 \hbar \pi c^3} |\mu|^2$, thus NSET

rate k_{NSET} follows [31]

$$k_{\text{NSET}} = 0.225 \cdot \frac{\Phi_D}{\omega_D^2} \cdot \frac{c^3}{\omega_F k_F d^4} \cdot \frac{1}{\tau_D} \quad (2.26)$$

where $c = 3.0 \times 10^8$ m/s is the speed of light, Φ_D is the quantum yield of the donor, τ_D^{-1} is the decay rate of the donor without the metal. NSET efficiency for a single donor-acceptor pair is expressed as

$$E_{\text{NSET}} = \frac{k_{\text{NSET}}}{k_{\text{NSET}} + \tau_D^{-1}} \quad (2.27)$$

d_0 , is termed as the “characteristic distance” and corresponds to the distance where the NSET rate equals the original decay rate of the donor without the metal or where the NSET efficiency, $E_{\text{NSET}} = 50\%$. Combining eq 2.26 and eq 2.27, yields,

$$d_0 = \left(0.225 \cdot \frac{\Phi_D}{\omega_D^2} \cdot \frac{c^3}{\omega_F k_F} \right)^{\frac{1}{4}} \quad (2.28)$$

$$E_{\text{NSET}} = \frac{1}{1 + \left(\frac{d}{d_0} \right)^4} \quad (2.29)$$

Compared with the d^{-6} distance dependence of the FRET efficiency shown in eq 2.7, which is $E_{\text{FRET}} = \frac{1}{1 + \left(\frac{d}{R_0} \right)^6}$, The NSET efficiency follows a d^{-4} distance dependence, which extends the energy transfer range.

In brief, the distance dependent energy transfer to Au NP can be grouped [30] into the FRET set ($n = 6$) and the NSET set ($n = 4$). Agreement of the FRET theory with the experimental reports has been found in Ref. [37, 44–48] while NSET theory in Ref. [29–31, 49, 50]. It raises a question that what is the nature behind the “inconsistent” distance dependent energy transfer to the Au NP? The possibility that the size of the Au NP possibly has an impact on the energy transfer mechanism has been recognized. Such as Griffin *et al.* investigated the distance dependence of energy transfer to the Au NP with the diameter of 8 nm, 40 nm and 70 nm respectively [158]. NSET model provides a better description of the distance dependence for the Au NP with a diameter of 8 nm but poor agreement for the Au NP with the diameters of 40 nm and 70 nm. However in different experimental reports, a better agreement of FRET formalism has been observed for the Au NP with the diameter of 5 nm in Ref. [47], 15 nm and 80 nm in Ref. [46]. To date most of the research concentrate on the study of the distance dependence, which are motivated by the application in nanosensors [26–28]. However, besides the size of the Au NP, the distance dependent

energy transfer is also dependent on other parameters, such as the spectral overlap of the donor emission and the LSP absorption of Au NP, the distance between the donor and Au NP, the ratio of the donor to the Au NP. Therefore, a systematic study of the energy transfer to the Au NP in one system but varying parameters is necessary in order to probe the nature of the energy transfer mechanism.

To the best of our knowledge this is the first study of the QD-Au NP energy transfer mechanism as a function of the QD-Au NP separation, donor emission wavelength as well as Au NP concentration in a planar geometry. The Au NP with an average diameter of 5.5 nm and five different sized QDs are selected. The QD emission peak wavelengths vary from 534 nm to 660 nm to probe the donor emission wavelength dependence. A planar geometry is used due to the well characterised layer distance. What is more important, the Au NP concentration or the ratio of the QD and Au NP can be varied as well, which has an impact on the energy transfer efficiency. By probing the distance, donor emission wavelength as well as Au NP concentration dependence in one system can give the guidance for the optimum conditions of an metal NP-fluorophore based nanosensor. The details of this study will be covered in **Chapter 4**.

2.3.3 Localised Surface Plasmon Mediated Energy Transfer

In 1980s, it has been theoretically proposed that LSP supported by metal NPs can modify FRET [52, 53] between two molecules, regarded as two point dipoles. The enhancement of the FRET strongly depends on the distance between the emitter and the metal NP, shape of the metal particle, and angular orientation of the molecules with respect to the metal NP. LSP coupled FRET decrease with the distance but can greatly extends the traditional FRET which is in the absence of the metal NPs, going up to ~ 70 nm. Govorov *et al.* proposed that the optimum geometry for the LSP mediated FRET, which has the strongest enhancement of the FRET rate, is to position the metal NP between donor-acceptor pair [54].

Experiments have verified that the enhancement of the energy transfer rate, efficiency, and range is achieved in different geometries with a variety of fluorophores and metal NPs. Lakowicz *et al.* firstly investigated the effect of silver island films on FRET between the donor DAPI (4',6-diamidino-2-phenylindole) and the acceptor PI (propidium iodide) [55]. An increase of the Förster radius from 3.5 nm to 16.6 nm is obtained when the bound donor-acceptor pairs are close to the silver film, which proved that the donor acceptor interaction strength can be enhanced by the metal NPs. Zhang *et al.* reported a 60% increase of a Förster radius by investigating energy transfer between a single donor-acceptor oligonu-

cleotide pair bound to a single silver NP [51, 56]. The FRET enhancement not only depends on the size of silver particle but also depends on the distance from the metal surface. Studying FRET from a conjugated polymer to fluorescent multilayer core-shell NP, Lessard-Viger *et al.* observed a 70% increase in the Förster radius and an increase in the FRET-rate by two orders of magnitude [57]. Not only limited to the isolated NPs, metal plasmonic nano-resonators can also enhance FRET, such as in the system with the donor R-phycoerythrin and acceptor Alexa Fluor 647 conjugates attached to Au NP dimers [58]. The other LSP enhanced FRET reports include donor ZnO NPs and acceptor CdSe/ZnS core-shell QDs with silver prisms in the spin coating layer [59]; other layered architectures such as mixed CdSe QDs layer with silver NPs layer [60]; mixed CdSe/ZnS and CdSe/ZnTe QDs with a Au NP layer [61] and also metallic NPs in planar structures [62–65].

Apart from the observations of the LSP enhanced FRET in the above examples, Wang *et al.* demonstrated that FRET could be switched on and off by varying the spectral position of the LSP resonance relative to the donor emission and acceptor absorption [66] through studying a core-shell geometry, composed of donor and acceptor fluorophore molecules embedded in a shell coating a Au-Ag core-shell nanocrystal. Further reports demonstrated the possibility to enhance [62] or inhibit [67] the energy transfer process in one geometry, which are reported in planar structures comprised of a layer of dyes and/or QDs, acting as donors and acceptors, placed on a metal NP layer. This depends on how the LSP coupled FRET rate competes with the decay rate of the donor species as well as the LSP modified decay rates of the donor species. The LSP modified decay rates of the donor or acceptor is verified by the fact that LSP can result in the PL quenching or enhancement [30, 40, 44, 154, 156, 159–161]. Furthermore, the donor-plasmon coupling or acceptor-plasmon coupling also has an effect on LSP mediated FRET, which was investigated by changing the order of the donor QD layers, acceptor QD layers and Au nanospheres layers in a multilayer stack [65].

As can be seen that the LSP coupled FRET process is quite complex due to the dependences on so many parameters, such as the spectral properties of the donor and acceptor, the spectral overlap of donor/acceptor emission and the surface plasmon resonance, the relative placement of the donor and acceptor within the near field of the plasmonic structure, the plasmonic field provided by metal NPs of different sizes [64], shape and the distance between the donor-acceptor pair and a metal NP layer [162].

Referring back to the beginning of this Section, LSP coupled FRET studies are motivated by extending the traditional FRET range or by improving the FRET efficiency for better FRET-based applications. It intrigues us that how we can experimentally control LSP

coupled FRET. A deep understanding of the mechanism or what kind of dependences of the LSP coupled FRET on varying parameters is necessary. In order for the systematic investigation of this process, LBL assembly is chosen for our study as we can precisely control and tune the parameters, such as Au NP concentration, layer separations. An acceptor QD-Au NP-donor QD multilayer is built, due to the proposed optimum geometry for the LSP coupled FRET [54]. The Au NP of 5.5 nm diameter is selected due to the negligible scattering, which excludes the emission enhancement of the donor and acceptors. So there is no competition between quenching and scattering effects and the signatures of LSP-coupled FRET are clearer. For example in this system any enhancement of the acceptor emission is a clear signature of energy transfer. More importantly, it enables us to study the effect of the LSP provided by Au NP monolayer on the donor or acceptor QD monolayer separately. Furthermore, we can study the LSP couple FRET process, such as FRET efficiency, rate as well as acceptor emission by tuning the Au NP concentration, the position of the intermediate Au NP monolayer by tuning donor QD-Au NP layer separation, acceptor QD-Au NP layer separation. These tunable parameters in one system enable us to study the various dependences and then can give us an insight of the LSP couple FRET process. Therefore, the systematic study of the LSP couple FRET is presented in in **Chapter 5**.

2.3.4 Localised Surface Plasmon in Quantum Well Pumping Quantum Dots

Quantum wells (QWs) are formed when sandwiching a narrow band-gap material between two layers of wide band-gap material. "Narrow" refers to the fact that QW width is smaller than electron de Broglie wavelength [163]. Quantized energy levels are derived and the energy levels are determined by the depth and thickness. III-V semiconductor QW has direct bandgap structure [163], which has shown promising prospects in optoelectric devices, such as light emitting diodes (LED), lasers, photovoltaics [164] due to its high electron and hole mobility, radiation resistance and high drift velocity [137].

QWs are a powerful pump platform for luminescent materials [15, 73, 74, 165, 166], playing an important role in optoelectronic devices such as colour converters [24, 71], light emitting diodes [72], and white light generation [18, 73]. The pumping is mainly based on radiative energy transfer, which is photon emission of QW, followed by re-absorption and emission in acceptors. However, it is limited by pumping photon losses due to nonradiative recombination channels and light outcoupling from the high refractive index to the low refractive index materials [137].

Basko *et al.* [165] theoretically predicted the feasibility of energy pumping from QW to organic molecules through nonradiative energy transfer or FRET. Achermann *et al.* experimentally developed the approach of efficient pumping *via* nonradiative energy transfer from InGaN/GaN QW to the proximal QDs layer and showed that FRET process is fast enough to compete with both radiative and nonradiative relaxation processes in the QW [15, 24]. The temperature and capping thickness dependent studies can be found in Ref. [167]. However, FRET is the near field dipole-dipole interaction while the efficiency is critically dependent on QW-QD separation. The proximal separation is a prerequisite in practical implementation to enable efficient pumping. Therefore, the capping layer should be as thin as possible to reduce the separation of QW and QDs. However, high energy transfer is limited by the thin capping layer. Thick capping layer is necessary to guarantee high carrier injection efficiency of QW, which can reduce the nonradiative losses [24]. Thus there are two competing factors, how can we obtain efficient energy transfer in QW-QD system to overcome the trade-off?

In order to solve this problem, many efforts have been devoted to enable efficient FRET from QW to QDs through optimization of architectures, such as dry-etched nanopillar [17, 74, 75] to obtained optimal interaction volume. Nizamoglu and coworkers reported a QW architecture deposited with graded QDs and achieved a FRET efficiency of up to 83% [74].

As the increase of FRET efficiency can also be realized with the aid of plasmonic coupling where the localized field created by plasmonic structure can enhance the strength of donor-acceptor interaction [52–54], can LSP enhance the energy transfer strength between QW and QD over longer distances? In **Chapter 6**, we aim to propose a new method based on LSP mediated FRET to solve the limited nonradiative energy pumping distance in QW-QD system. Thus the QW-Au-QD system is built where Au NP monolayer is positioned between QW and QD monolayer to compare with Au-absent QW-QD system. This has potential for QW applications as the pumping platform with enhanced energy transfer efficiency or over large distances. Furthermore, motivated by the potential of incorporating QW into on-chip nanostructures for applications in optoelectronic and biophotonic devices [168], the energy transfer to the Au NP will also be probed. The energy transfer efficiency dependence on separation by tuning QW's capping thickness has been reported elsewhere [168]. The Au NP concentration dependent energy transfer will be studied.

Chapter 3

Sample Preparation and Characterisation

"Core-only" type CdTe Quantum Dots (QDs) are used in this thesis. QDs are stabilised by thioglycolic acid (TGA), the synthesis procedures can be found in Ref. [169–171] and are negatively charged. QDs are obtained from Prof. Yurii Gun'ko group in the school of Chemistry of Trinity College Dublin and from Dr. Vladymir Lesnyak and Dr. Nikolai Gaponik from the Technical University in Dresden, Germany. Colloidal Au nanoparticles (NPs) with an average diameter of 5.5 nm are obtained from Dr. Andrei Sussha and Prof. Andrey Rogach from City University of Hong Kong. The Au NPs are stabilized by 4-dimethylaminopyridine (DMAP) [172], which are positively charged. Both QDs and Au NPs are water soluble and thus suitable for the water-based assembly method. The charged properties of QDs and Au NPs enable us to use layer-by-layer (LBL) approach [70, 173] to form complex layered structures. The QD or Au NP monolayer, QD-QD, QD-Au NP bilayer or QD-Au NP-QD trilayer samples investigated in this thesis are all prepared by LBL approach. The basics of LBL approach, the sample characterisation methods, as well as Förster resonance energy transfer signatures are shown in this Chapter.

3.1 Layer-by-Layer Assembly

3.1.1 Principle

LBL can date back to Iler's work in 1966 [174], which was then revived and established by Decher and co-workers [68–70]. It is a versatile bottom-up nanofabrication technique, which has become one of the most preferred techniques for thin films preparation and has

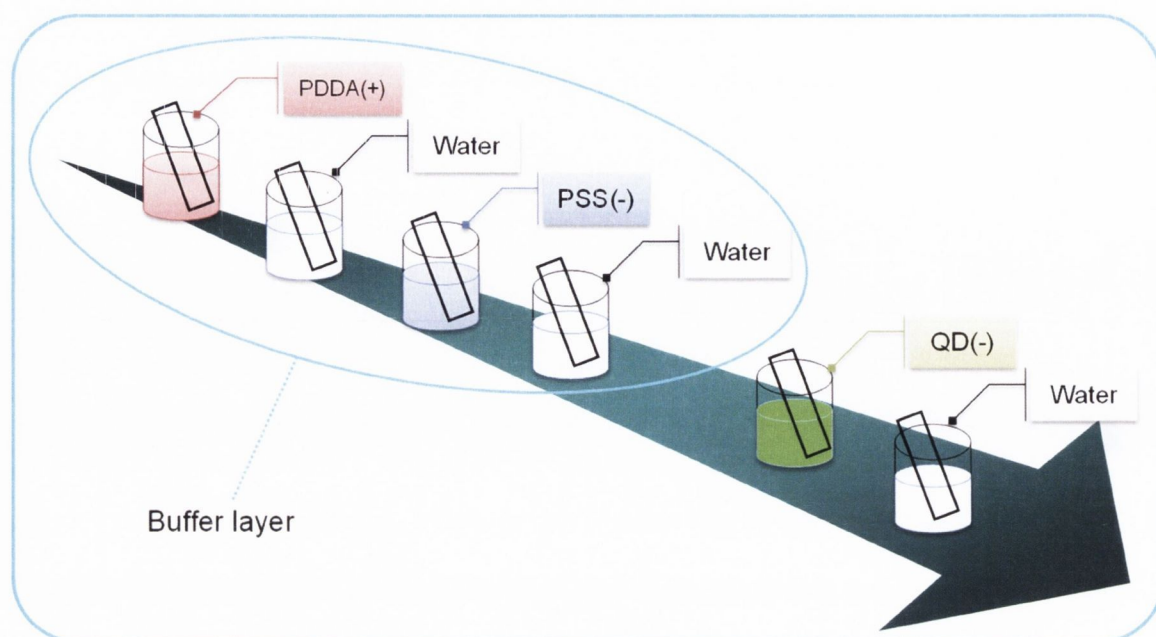


Fig. 3.1 Schematic of LBL process, PDDA is positively charged while PSS is negatively charged. TGA-capped CdTe QDs are negatively charged. Four bilayer of PDDA/PSS are deposited as buffer layer.

been practiced by numerous research groups worldwide.

The basic principle is electrostatic attraction of oppositely charged polyelectrolytes (PEs). The inversion of zeta potential of charged colloids after adsorption of an oppositely charged PE had been experimentally observed [70]. The common positively charged PE are poly (allylamine hydrochloride) (PAH), polyethyleneimine (PEI) and poly (diallyldimethylammonium chloride) (PDDA); The common negatively charged PE are poly(sodium styrene sulfonate) (PSS), poly (acrylic acid) (PAA) and poly (vinyl sulfate).

The general process (PDDA-PSS pair) is illustrated in Fig. 3.1. By sequential dipping of a pre-treated charged substrate in the oppositely charged solution (positively charged PDDA; negatively charged PSS), a multilayer PE film is formed. Rinsing by millipore water after each dipping is necessary in order to remove loosely bound PEs. The roughness and thickness can be controlled at the molecular level upon adjusting experimental parameters such as salt/polyelectrolyte concentration, and immersion time. A variety of inorganic nanomaterials are available for the LBL which has led to an exceptional growth in the fabrication of LBL composites, such as NPs [175], nanosheets [176], and nanowires [177], nanoplates [178] and organic (dendrimers, polypeptides [179], DNA [180], and proteins [181].

To provide the charged property for the substrate, the quartz (12 cm × 10 cm × 1.5 mm) substrate is immersed with sonication in the following solution sequentially:

- Millipore water for 10 min,
- 1 M NaOH (4-5 g of NaOH in 75 ml millipore water) for 15 min,
- Ethanol + NaOH (4-6 pellets in Ethanol) for 15 min,
- Fresh millipore water for 10 min.

Then the substrate has a slightly negative native surface charge, which yields possibility for subsequent LBL. The procedure can be seen in Fig. 3.1 as

- The quartz substrate is immersed in the positively charged PDDA solution for 10 min, then rinsed with millipore water for 1 min to remove loosely adsorbed polyelectrolytes.
- It is dipped into the negatively charged PSS solution for 10 min, and then rinsed with fresh millipore water for 1 min.
- Four bilayers of PDDA/PSS will be built as buffer layer before deposition of NPs.
- After the deposition of the PE layer, the sample was then immersed in an aqueous solution containing the NPs.

The concentration of the NP solution and immersion time will determine the final NP concentration in a monolayer. With consideration for the uniformity and reproducibility, the quartz substrate treatment and deposition conditions are kept constant, such as PDDA/PSS solution, PH and salt concentration. Furthermore, the longer immersion times lead to more reproducible results [70]. To prevent cross-contamination of deposition solutions, large volume fresh millipore water is used for rinsing. As mentioned earlier, PDDA and PSS depositions are repeated consecutively to build the buffer layer. The influence of the substrate vanishes after a few deposition cycles and finally the optical properties of the NP monolayers are not influenced by quartz but only the PE layers [70].

The chemicals used are obtained from Sigma Aldrich. A 20wt% solution of PDDA in water, with a molecular weight of 100,000 to 200,000 is used as PDDA stock solution. 543 ml PSS powder (with a molecular weight of approximately 70,000) is dissolved in 10ml millipore water is used as PSS stock solution.

The recipes for 0.1 M PDDA/PSS solution for LBL are

PDDA 170 μ L PDDA stock+0.2 ml NaCl (3 M) +5.8 ml millipore water.

PSS 560 μ L PSS stock +0.2 ml NaCl (3 M) +5.3 ml millipore water.

The recipes for 0.5 M PDDA/PSS solution for LBL are

PDDA 170 μ L PDDA stock+1ml NaCl (3 M) +5 ml millipore water.

PSS 560 μ L PSS stock+1ml NaCl (3 M) +4.5 ml millipore water.

3.1.2 Measurement of Polyelectrolyte Thickness

The sample with varying layer thickness of PDDA/PSS is recorded by UV-Vis spectroscopy measurement. The absorption spectra of four bilayers of PDDA/PSS is shown in Fig 3.2 (a), the inset shows clearly a band at 266 nm originated from PSS. In Fig 3.2 (b), the absorption value (left axis, blue solid square and red open circles) at 266 nm as a function of different number of PE layers are plotted. Some samples were measured using X-Ray diffraction and the measured thickness (right axis, green open squares) is also presented. The linear fit ($\chi^2 \approx 0.99$ for both cases) of the absorption versus the number of PE layers indicates that the PE thickness could be well controlled by adjusting the number of PE layer. There is a slight deviation for the 1BL PE with 0.1M NaCl, possibly due to the weak original charge surface before deposition. The multilayer samples in this thesis are always deposited on a 4BL PDDA/PSS PE as buffer layer. A single bilayer of PDDA/PSS with 0.1 M NaCl concentration has average thickness of ≈ 3 nm while 0.5 M NaCl concentration has a thickness of ≈ 7 nm.

3.2 Experimental Characterisation

All the absorption spectra of samples are recorded using a double-beam UV-Vis spectrometer (Shimadzu UV-2401PC). Room temperature steady state photoluminescence spectra were measured with a Perkin-Elmer LS 55 fluorescence spectrometer using an excitation wavelength of 400 nm, provided by a pulsed Xeon lamp. The time-resolved PL decays are measured by a PicoQuant Microtime 200 time-resolved confocal microscope system with an excitation wavelength of 470 nm or 400 nm using $40\times$ objectives. PL decays are measured over an area of $80\ \mu\text{m}\times 80\ \mu\text{m}$ with integration time of 4 ms per pixel. Each sample is deposited on both sides of the quartz slides, measured at different positions to check the uniformity. All the data presented in the thesis are calculated from the average value and the variation is included in the error bars.

3.2.1 Absorption Measurement

Consider incident monochromatic light with power I_0 propagating along the x direction and passes through a homogeneous medium with thickness, l , shown in Fig 3.3. The excitation light spot area is A and the light intensity decreases from left to the right with the attenuation constant σ . The concentration of the sample is C , after passing through the medium the light intensity becomes I .

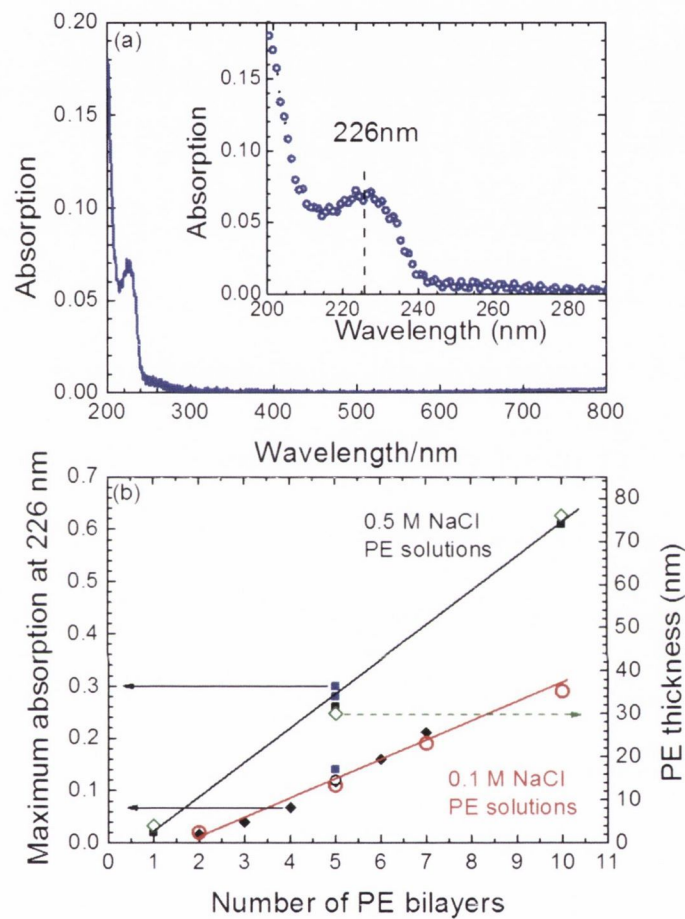


Fig. 3.2 (a) Absorbance of four bilayers of PDDA/PSS containing 0.1 M salt concentration on quartz. The band at 226 nm originated from the PSS. (2) The absorption value at 266 nm (left axis, blue solid squares and open red circles) and the thickness of several samples (right axis, open green squares) as a function of number of (PDDA/PSS) layers. PE layers containing 0.1 M and 0.5 M salt concentration are shown respectively. The solid lines are the linear fit of the absorption. (The absorption vs thickness has been established by Robert Gunning (X-Ray diffraction measured thickness, green open squares) and Manuela Lunz (absorption data, blue solid squares) [182]. The absorption of the LBL samples in this thesis are shown as open red circles, and can be read on the right axis directly.)

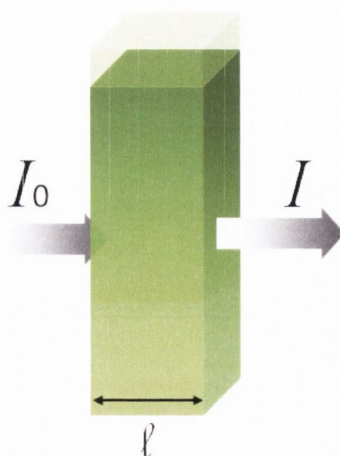


Fig. 3.3 Incident light intensity before I_0 and after I passing through homogeneous sample with the thickness l .

As the fractional decrease for a solution depends linearly on the number of the absorbing species (such as molecules, QDs), the fractional change in light intensity can be written as [183]

$$-\frac{dI_x}{I_x} = \frac{\sigma CA}{A} dx \quad (3.1)$$

when dx is sufficiently small,

$$\int_{I_0}^I \frac{dI_x}{I_x} = \int_0^l -\frac{\sigma CA}{A} dx \quad (3.2)$$

As neither σ nor concentration C depends on x ,

$$\ln \frac{I}{I_0} = -\sigma Cl \quad (3.3)$$

$$I(\lambda) = I_0(\lambda) e^{-\sigma Cl} \quad (3.4)$$

The transmitted light intensity I decrease exponentially with increasing light path and increasing concentration. The absorption, absorbance or optical density, A is not defined using

natural logarithm but as

$$\begin{aligned}
 A &= \log\left(\frac{I_0(\lambda)}{I(\lambda)}\right) \\
 &= \log\left(\frac{I_0(\lambda)}{I_0(\lambda)e^{-\sigma Cl}}\right) \\
 &= \log(e^{\sigma Cl}) \\
 &= Cl\sigma \cdot \log(e) \\
 &= \epsilon Cl
 \end{aligned} \tag{3.5}$$

where $\epsilon = \sigma \cdot \log(e) = \sigma/2.303$ is the molar absorption coefficient or molar absorptivity (molar extinction coefficient) in units of $\text{M}^{-1}\text{cm}^{-1}$ while C is in units of molarity M and the path length is in units of cm . Eq. 3.5 is known as the Lambert-Beer law.

The difference of light intensity before (I_0) and after (I) passing through sample (Fig. 3.3) results from absorption, reflection at the sample holder windows and the absorption of the solvent. To obtain pure absorption signal from the solute, the setup is baselined by the same sample holder with the solvent only (such as, a cuvette containing water is used to obtain the baseline for measuring absorption spectrum of water-soluble CdTe QDs).

If the sample is a mixture of many elements N , the absorption spectra of the sample A is a mixture of elements $(1, 2, \dots, N)$ with varying absorption spectra as

$$A = A_1 + A_2 + \dots + A_N = l \sum_i C_i \epsilon_i \tag{3.6}$$

where C_i , ϵ_i are the concentration, extinction coefficient of the element i in the sample holder.

3.2.2 Steady-state Photoluminescence Measurement

The steady-state absorption as well as photoluminescence (PL) spectra of the QD solution are shown in Fig 3.4, the emission peak is centred at $\lambda_{em} = 550 \text{ nm}$ or 2.25 eV while the $1s-1s$ absorption peak A_{1s-1s} is at 524 nm or 2.36 eV . The energy difference between the absorption and emission peak is 110 meV , which is the "Stokes shift". The full width at half maximum (FWHM) is 38.9 nm (156 meV). The QD size distribution is given by

$$\frac{\text{FWHM}}{E_{em}} = \frac{153 \text{ meV}}{2.25 \text{ eV}} = 6.8\% \tag{3.7}$$

The average QD diameter D can be estimated from the sizing curve as a function of $1s-1s$ absorption peak. For TGA-capped CdTe QDs [171, 184] which we use in this thesis,

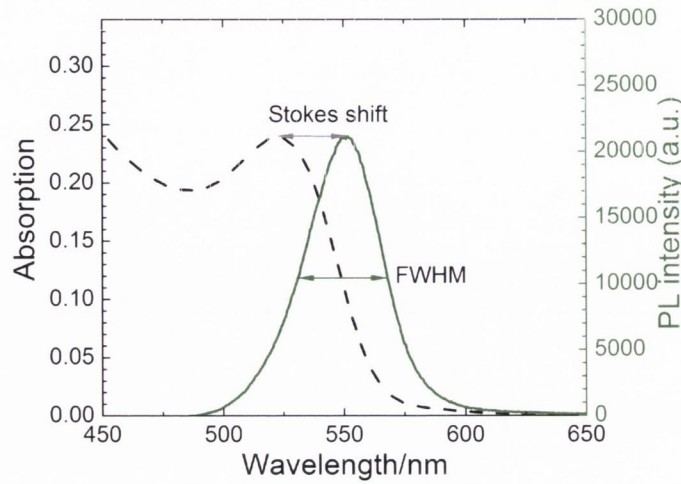


Fig. 3.4 Absorption (black dash line) and emission at $\lambda_{ex} = 400$ nm (red solid line) of QDs solution, the arrow shows PL full width at half maximum (FWHM) and Stokes shift.

the empirical sizing curve is

$$D = (9.8127 \times 10^{-7})\lambda_{1s-1s}^3 - (1.7147 \times 10^{-3})\lambda_{1s-1s}^2 + 1.0064\lambda_{1s-1s} - 194.84 \quad (3.8)$$

The extinction coefficient of QDs ϵ_{QD} could be correspondingly determined by

$$\epsilon_{QD} = 10043(D)^{2.12} \quad (3.9)$$

As seen in Fig 3.4, $A_{524} = 0.24$ is the measured absorption at $1s - 1s$ peak, Therefore,

$$\begin{aligned} D &= 2.6 \text{ nm}; \\ \epsilon_{QD} &= 9.465 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}; \\ C_{QD, \text{Sol}} &= \frac{A}{\epsilon_{QD} \cdot l} = 3.38 \times 10^{-6} \text{ M} \end{aligned} \quad (3.10)$$

where l is the length of the cuvette with $l = 1$ cm, $C_{QD, \text{Sol}}$ is the molar volume concentration of the solution as mol/L.

Based on absorption and emission measurements, the quantum yield (QY) of QDs could be obtained by comparison with standard samples with a well-characterised QY [185] such as Rhodamine 6G dispersed in ethanol with a QY of 95%. Under identical excitation and detection conditions, the absorption and emission of QD solution and dye is shown in Fig 3.5.

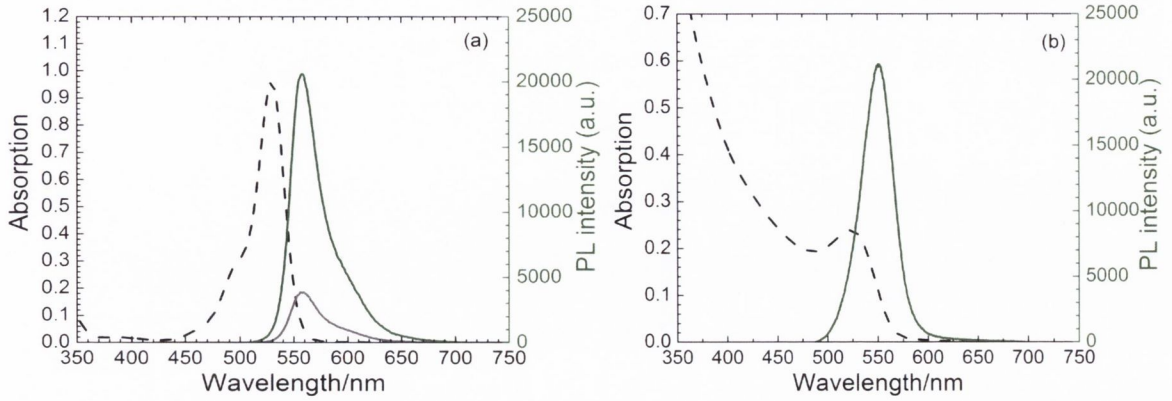


Fig. 3.5 Absorption (dash line) and emission at the excitation wavelength of $\lambda_{ex} = 400$ nm (green solid line) and at $\lambda_{ex} = 475$ nm (grey line) of (a) dye solution and (b) QD solution.

The QY is calculated as

$$\Phi_{QD,Sol} = \left(\frac{A_{ref}(\lambda_{ex})}{A_{QD}(\lambda_{ex})} \right) \left(\frac{I_{QD}}{I_{ref}} \right) \left(\frac{n_{QD}}{n_{ref}} \right)^2 \Phi_{ref} \quad (3.11)$$

where Φ is the QY, A is absorption value at the excitation wavelength λ_{ex} , I is the integrated emission intensity, and n is the refractive index of the solvent. Subscripts ref and QD refer to the standard and QD samples, respectively.

$$\Phi_{QD,Sol} = \left(\frac{0.0167}{A_{Sol}(\lambda_{ex})} \right) \left(\frac{I_{Sol}}{163563} \right) \left(\frac{1.333}{1.329} \right)^2 \cdot 0.95 = 20.7\% \quad (3.12)$$

The absorption and normalised PL spectra of the QD solution and layer are shown in Fig 3.6 (a) and (b), respectively. The absorption of the monolayer could be scaled linearly by that of the solution, the indistinguishable absorption shape of monolayer and solution indicates that the extinction coefficient does not change in both media. However, the PL emission of QD layer shows a red shift with respect to QD solution, which results from intra-energy transfer from smaller sized QDs to larger sized QDs. The QY of the QD monolayer is calculated by

$$\Phi_{QD,ML} = \left(\frac{0.0167}{A_{ML}(\lambda_{ex})} \right) \left(\frac{I_{ML}}{163563} \right) \left(\frac{1.5}{1.329} \right)^2 \cdot 0.95 \cdot \frac{0.7}{0.5} \approx 4\% \quad (3.13)$$

where $n_{QD} = 1.5$ is the refractive index for the ligand and surrounding PEs. $\frac{0.7}{0.5}$ is included to take into account of the contributions of the QD layer at the front and back sides of the sample.

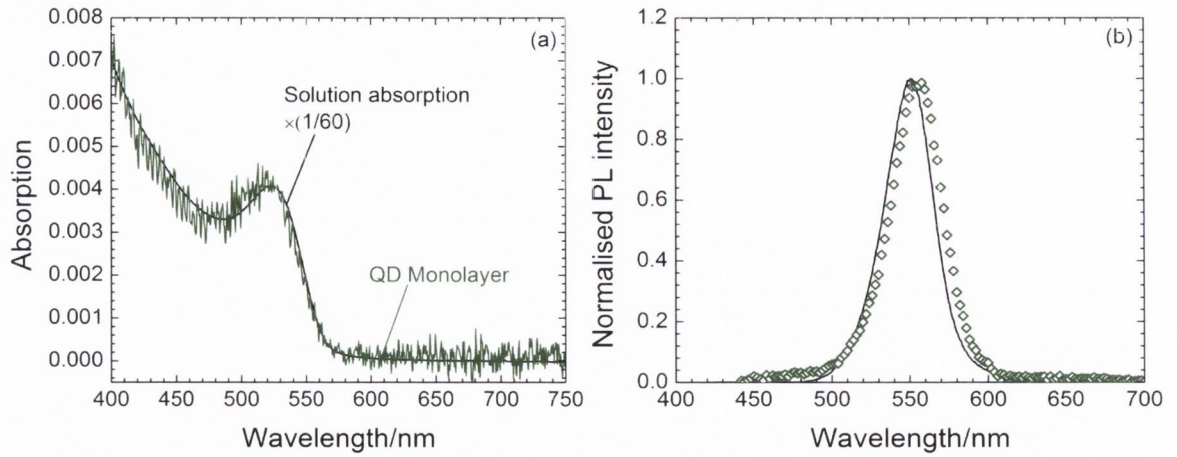


Fig. 3.6 (a) Absorption and (b) normalised PL intensity of QDs solution (black) and monolayer (green).

The QD concentration in monolayer $C_{\text{QD,ML}}$ is calculated following the method in Ref. [182] as

$$\begin{aligned}
 C_{\text{QD,ML}} &= \frac{A_{\text{ML}}}{A_{\text{Sol}}} \cdot C_{\text{QD,Sol}} \cdot \frac{1 \text{ cm}}{d_{\text{QD}}} \cdot \frac{1}{2} \cdot N_A \cdot 10^3 \cdot \frac{1}{m^3} \cdot d_{\text{QD}} \\
 &= \frac{A_{\text{ML}}}{A_{\text{Sol}}} \cdot C_{\text{QD,Sol}} \cdot 3.011 \times 10^{24}
 \end{aligned} \tag{3.14}$$

where $\frac{A_{\text{ML}}}{A_{\text{Sol}}}$ is the ratio of the absorption value at 1s-1s peak. $N_A \cdot 10^3 \cdot \frac{1}{m^3} \cdot d_{\text{QD}}$ is multiplied to convert the concentration from solution to surface density. N_A is the Avogadro constant. $\frac{1}{2}$ is multiplied as QD are deposited on both sides of the quartz substrate. Thus, the QD monolayer in Fig 3.6 (a) has a concentration $C_{\text{QD,ML}} = 1.7 \times 10^{17} \text{ m}^{-2}$.

3.2.3 Time-resolved Photoluminescence

Following a short excitation pulse of light, the emission intensity is recorded as a function of time. The time-dependence of the PL can be expressed as

$$I(t) = I_0 + \sum_{i=1}^n A_i e^{-\frac{t}{\tau_i}} \tag{3.15}$$

where,

I_0 is the background of the measurement,

τ_i represents the characteristic time of the i th decay component,

A_i are the amplitudes for each decay component.

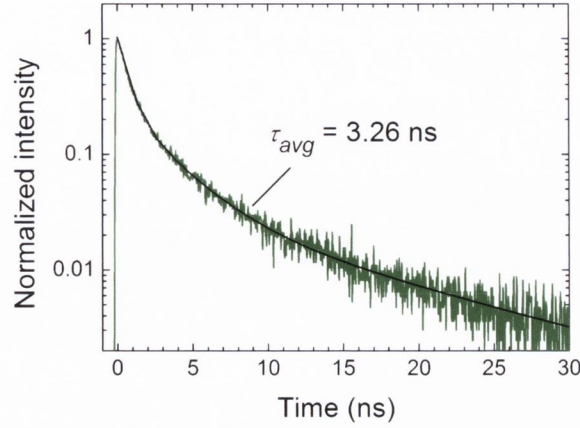


Fig. 3.7 Time-resolved photoluminescence decay of QD monolayer (green) recorded with 500 nm filter (the transmission profile could be found in Fig 3.8). The black line is the fit using the two exponential method based on eq 3.16.

As shown in Fig 3.7, a normalized PL decay curves are fitted by a bi-exponential function

$$I(t) = I_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (3.16)$$

where A_1, A_2 are the amplitudes and τ_1, τ_2 are the fast and slow decay components respectively. The amplitude weighted average lifetime is calculated as

$$\tau_{\text{avg}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (3.17)$$

The fitting parameters of the example in figure is

$$A_1 = 0.8309, \tau_1 = 0.725;$$

$$A_2 = 0.1861, \tau_2 = 4.926.$$

yielding an average lifetime of $\tau_{\text{avg}} = 3.26$ ns with $\chi^2 = 0.997$.

3.3 Förster Resonance Energy Transfer in Quantum Dot Monolayer

A QD monolayer is the basic unit of QD architecture by LBL. Here we characterise the optical properties of QD monolayers with varying QD concentration and demonstrate the analysis of the FRET mechanism. Furthermore, QD monolayers are built as the reference samples to compare with complex geometries, such as QD-gold NP bilayer in Chapter 5 and trilayer structures with intermediate Au NP monolayer in Chapter 6.

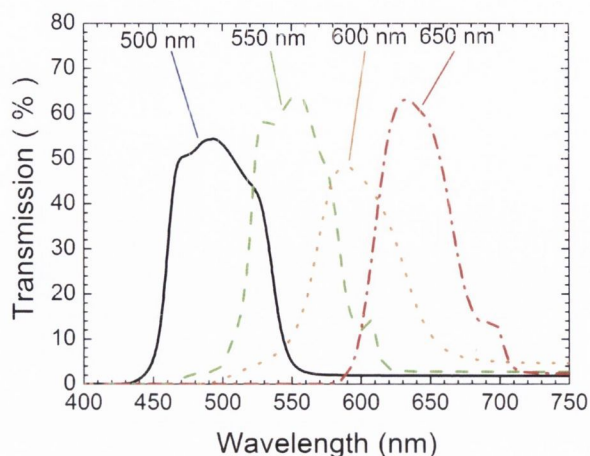


Fig. 3.8 Transmission spectra of broad band filters with central wavelengths of 500 nm, 550 nm, 600 nm, 650 nm.

3.3.1 Förster Resonance Energy Transfer Signatures

The spectrally integrated emission intensity of monolayers with varying QD concentration is presented in Fig 3.9 (a). The linear increase of the intensity with concentration indicates that the QY of QD monolayer keeps constant. The QY is calculated to be 4% based on the eq 3.13. The concentration dependent decay lifetime τ_{blue} , which is recorded on the blue side of the QD monolayer with a 500 nm broadband filter, the transmission spectra of the filters are shown in Fig 3.8.

The lifetime yield in Fig 3.9 (b), which is the ratio of the concentration dependent lifetime τ_{blue} over the single QD lifetime τ_0 , decreases with increasing QD concentration. $\tau_0 = 19$ ns, which is the decay lifetime of the sample with the very low QD concentration, which is the donor lifetime without FRET [127]. The reduction of the lifetime yield is attributed to intra-ensemble energy transfer within the QD monolayer, where the energy transfers from the blue side (smaller size QD) to the red side (larger size QD) of the QD ensemble. Both Dexter transfer and FRET can result in the decrease of the decay lifetime. However, the minimum distance between QDs is centre-to-centre distance including QD diameter ($D = 2.7$ nm) as well as the ligand thickness (~ 0.5 nm), which is much larger than the Dexter transfer distance ~ 1 nm and therefore Dexter transfer can be excluded.

3.3.2 Theoretical Analysis

The energy transfer in monodispersed QD monolayers has been investigated and the details can be found in Ref. [127]. The lifetime yield τ_{blue}/τ_0 , is the ratio of the concentration

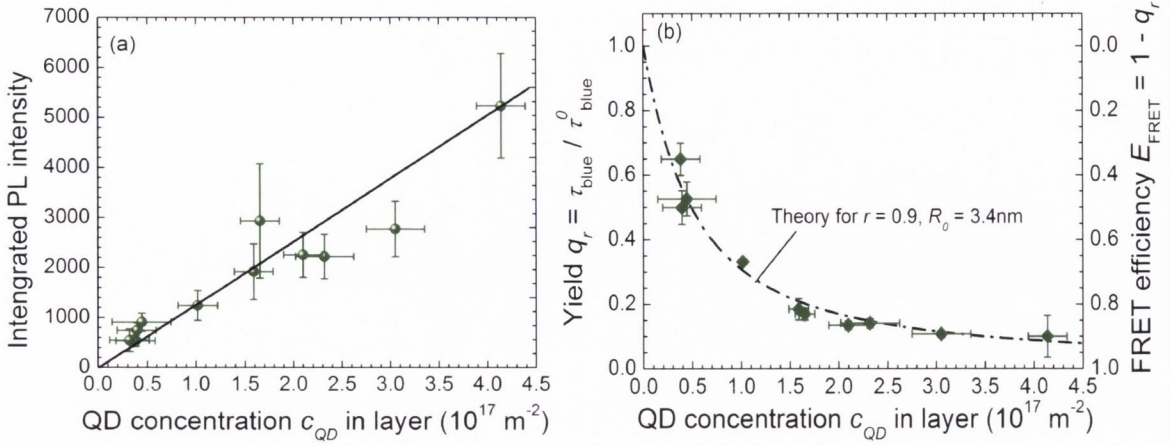


Fig. 3.9 (a) QD concentration dependence of the integrated emission intensity of QD ensemble. (b) QD concentration dependence of the lifetime yield measured on the blue side of the ensemble emission spectrum.

dependent lifetime τ_{blue} and an undisturbed value τ_0 . The undisturbed value can be obtained from QD monolayer with the lowest concentration where QD in monolayer behaves a single QD without any other QDs in close proximity. τ_{blue}/τ_0 can be modeled as

$$q_r = \frac{\tau_{blue}}{\tau_0} = \int_0^\infty e^{-\lambda} e^{-\pi c \gamma(2/3, \frac{\lambda}{r}) \lambda^{1/3}} \times e^{\pi c r^{1/3} (1 - e^{-\lambda/r})} d\lambda \quad (3.18)$$

where $\gamma(x, y) = \int_0^y z^{x-1} e^{-z} dz$ is the incomplete Gamma function, $c = C_{QD} R_0^2$ is a dimensionless concentration of the QDs, $\gamma = \frac{d}{R_0}$, $d = 2 \times r_{QD} + 0.5$ is the minimum centre-to-centre distance between QDs in densely packed monolayer including the ligand thickness $\sim 0.5 \text{ nm}$ [127]. $R_0 = 3.4 \text{ nm}$ is obtained from the model shown as the dash line in Fig 3.9 (b).

Furthermore, as seen in Fig 3.4, there is spectral overlap of the area-normalised QD emission and its absorption. R_0 can also be calculated from FRET theory as discussed in Sect. 2.2.1, Chapter 2. The spectral overlap J and Förster radius can be calculated by

$$R_0 = 0.0211 \left[\frac{\kappa^2 \Phi_D J(\lambda)}{n^4} \right]^{\frac{1}{6}} \text{ with } J(\lambda) = \int_0^\infty \hat{f}_D(\lambda) \cdot \epsilon_D(\lambda) \cdot \lambda^4 d\lambda$$

Therefore, $R_0 = (3.4 \pm 0.3) \text{ nm}$ is obtained. The agreement of R_0 from experimental observations and that calculated from spectral overlap demonstrates that there is intra-energy transfer in QD monolayer and the energy transfer is mediated by dipole-dipole interaction.

As there is intra-energy transfer in QD monolayer, which is dependent on the QD concentration, QD concentration is always kept the same in the reference and control sample.

Such as in Chapter 4, QD monolayer is the reference sample, which will be compared with QD-Au NP bilayer, the QD concentration is kept the same in both structures to exclude the influence of the intra-energy transfer.

3.4 Colloidal Au Nanoparticle

3.4.1 Extinction, Absorption and Scattering

In order to determine the Au NP concentration in a monolayer or in complex layer structures from Lambert-Beer law, such as bilayer or trilayer, the extinction cross section of Au NP needs to be derived. The extinction, absorption and scattering cross section of an isolated colloidal Au NP, σ_{ext} , σ_{abs} and σ_{sca} , for a spherical particle can be derived from Mie theory, the details can be found in Ref. [159, 186, 187]. Based on the Mie theory, the UV-visible absorption spectra of a fairly dilute dispersion of colloidal particle can be calculated from the absorption cross section as [188]

$$A = N\sigma_{\text{abs}}L/\ln 10 \quad (3.19)$$

where N is the the number of the Au NP per volume, L is the optical path length respectively. This equation has been validated to explain the absorption spectra of small metallic NPs (< 20 nm) in a qualitative and quantitative manner. By the comparison of the measured and calculated absorption, an extinction cross section of $\sigma_{\text{Au}} = 4.53 \text{ nm}^2$ is derived at LSP absorption peak ~ 518 nm as shown in Fig 3.10, corresponding to an extinction coefficient of $1.1 \times 10^7 \text{ M}^{-1}\text{cm}^{-1}$. However, for the actual synthesized colloidal Au nanospheres, there are size distributions or even some non-spherical NPs. Both the extinction cross section and extinction coefficient values depend crucially on the real size of the Au NPs, the size distribution and even some non-spherical particles. There are possible derivations with the actual value of the extinction cross section, which needs more sophisticated calculations. Furthermore, the refractive changes from the Au NP solution to the Au NP layer, which will also has an effect on the extinction cross section. In this thesis, we use a single Au NP stock solution for all the samples investigations, so we use the extinction cross section of the solution throughout. Au NP concentration is only used to compare the Au NP concentration in different samples without any interpreting this data.

Furthermore, the absorption and scattering extinction cross sections of 5.5 nm diameter Au NP are also shown in Fig 3.10, calculated from Mie theory. The scattering is almost negligible compared to absorption, the absorption cross section is approximately equal to the

extinction cross section as $\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$. Due to negligible scattering, the enhancement should not play a significant role in the excited decay process for a QD near a metal NP [147].

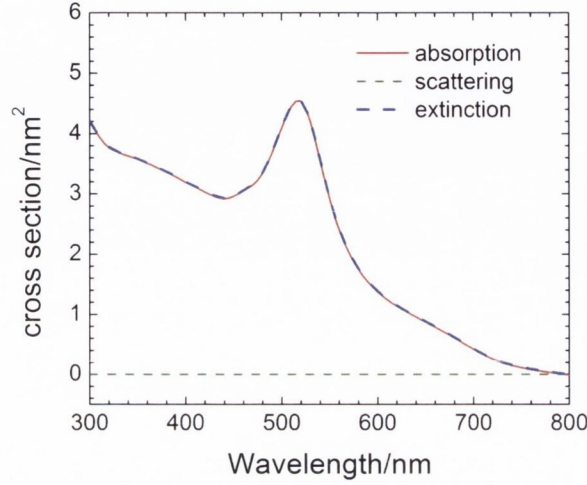


Fig. 3.10 Extinction, scattering and absorption cross section of a Au NP with a diameter of 5.5 nm. The refractive index of the environment is 1.33 for water.

3.4.2 Au Nanoparticle Concentration

Fig 3.11 shows the absorption spectra of Au NP dispersed in water (a) as well as that of monolayer (b). The LSP absorption peak of Au NP in solution is at ~ 518 nm, which agrees with the Mie calculation. The LSP absorption peak shows a red shift in the monolayer, which is centred at ~ 532 nm due to refractive index changes. The concentration of Au NP solution in Figure 3.11 (a) is derived from Lambert-Beer law as

$$C_{Au,Sol} = \frac{A_{Au,Sol}}{\epsilon_{Au} \cdot l} = 1.45 \times 10^{-6} M \quad (3.20)$$

Suppose the extinction of Au NP ϵ_{Au} does not change from solution to layer, similarly as QD concentration calculation by eq 3.14, the concentration of Au NP monolayer is roughly calculated as

$$C_{Au,ML} = \frac{A_{Au,ML}}{1.1 \times 10^7} \cdot \frac{1}{2} \cdot 6.022 \times 10^{24} m^{-2} \quad (3.21)$$

Therefore, the concentration of Au NP monolayers shown in Fig 3.11 (b) has the concentration ranging from $0.02 \times 10^{17} m^{-2}$ to $0.13 \times 10^{17} m^{-2}$. In order to determine the QD or Au

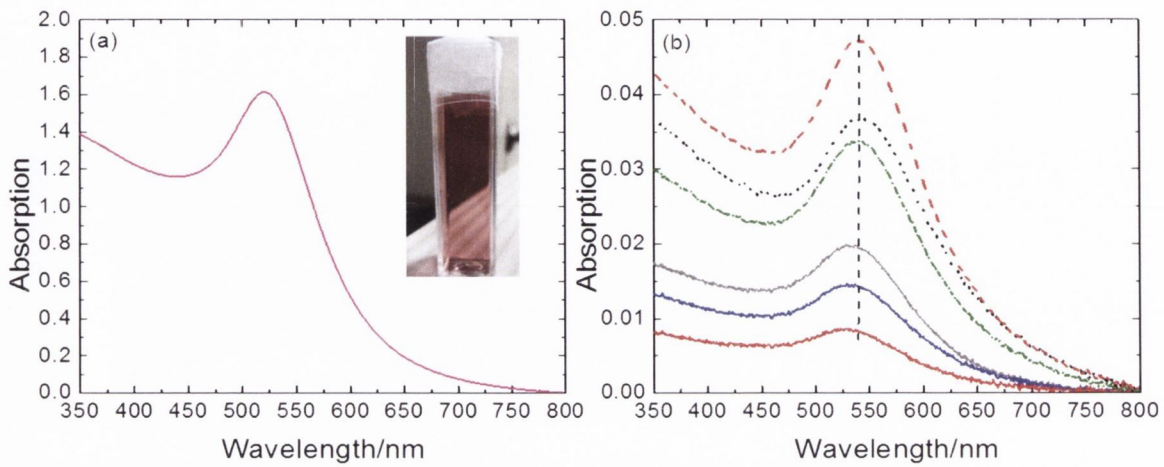


Fig. 3.11 (a) Absorption spectrum of a Au NP solution with concentration of 1.45×10^{-6} M. Inset shows the image of the Au NP solution in a cuvette. (b) Absorption spectra of Au NP monolayers with varying concentration $C_{Au,ML} = 0.02 \times 10^{17}m^{-2} - 0.13 \times 10^{17}m^{-2}$.

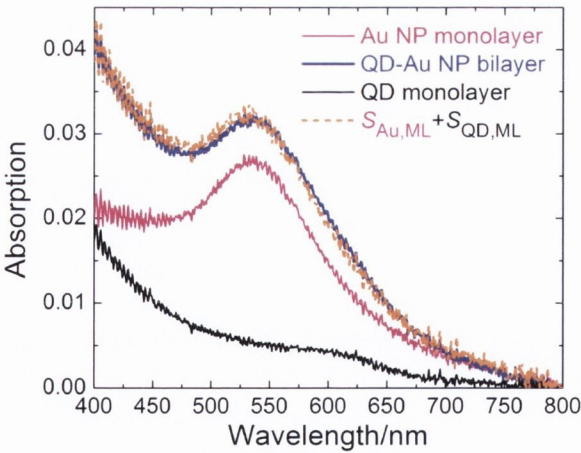


Fig. 3.12 Absorption spectra of QD monolayer (black solid line), Au NP monolayer (pink solid line), QD-Au NP bilayer (blue solid line) as shown, from which the absorption spectrum of PEs has been subtracted. The orange dash line is the superposition of absorption spectrum of Au NP monolayer $A_{Au,ML}$ and QD monolayer $A_{QD,ML}$.

NP concentration in complex structures, such as bilayer or trilayer samples, the monolayers are built as reference samples. As shown in Fig 3.12, the QD monolayer has a concentration of $2.10 \times 10^{17} \text{m}^{-2}$, the Au NP monolayer has a concentration of $0.071 \times 10^{17} \text{m}^{-2}$. The absorption spectrum of QD-Au NP bilayer is shown as blue line, which can be obtained by superposition of the absorption spectra of QD monolayer $A_{\text{QD,ML}}$ and Au NP monolayer $A_{\text{Au,ML}}$ as

$$A_{\text{QD-Au}} = \gamma_1 \times A_{\text{QD,ML}} + \gamma_2 \times A_{\text{Au,ML}} \quad (3.22)$$

γ_1 , γ_2 are parameters to scale with the absorption of reference QD and Au NP monolayer to take into account the slight differences with the reference samples. The slight differences possible result from the rinsing speed controlled by hands after each dipping step [70], as all the other depositions and measurements have kept as constant as possible. The dash line is the superposition using eq 3.22 with $\gamma_1 = 0.98$, $\gamma_2 = 1.1$. It can be seen that the spectrum of QD-Au NP bilayer can be reproduced by the sum of the absorption spectrum of QD monolayer and Au NP monolayer with slight different weighting factors. Therefore, the accurate QD concentration in the bilayer sample is $2.06 \times 10^{17} \text{m}^{-2}$ while Au NP concentration in the bilayer sample is $C_{\text{Au}} = 0.078 \times 10^{17} \text{m}^{-2}$. The reference samples and control samples are always built using similar LBL deposition conditions, such as solution concentration, immersion time. The values of γ_1 , γ_2 are always close to 1.

Similarly, the absorption spectrum of the trilayer sample can be fitted by the absorption spectra of donor QD monolayer, acceptor monolayer and Au NP monolayer with three fitting parameters. The straightforward way for the determination of the concentrations is to prepare an Acc QD-Au NP-Don QD trilayer sample sequentially shown below, the sample is left to dry in air at each step and then take the absorption as

1. the quartz substrate+PE, take the absorption spectrum, name as A_1 ,
2. the quartz substrate+PE+Acc QD, take the absorption spectrum, name as A_2 ,
3. the quartz substrate+PE+Acc QD+PE+Au NP, take the absorption spectrum, name as A_3 ,
4. the quartz substrate+PE+Acc QD+PE+Au+PE+Don QD, take the absorption spectrum, name as A_4 .

At each step, similar QD or Au NP monolayer is also prepared as the reference samples. A_3 , A_4 as well as the spectrum of donor QD monolayer can be used to determine the donor QD concentration in the complex structures. A_2 , A_3 together with the spectra of Au NP monolayer, QD monolayer can be used to determine the Au NP and QD concentrations in the complex structures as discussed earlier.

3.5 Conclusion

In conclusion, we have presented in this Chapter how we prepared the samples studied in this thesis with controllable QD or Au NP concentration and layer distance through LBL. It enables us the investigation of the Au NP concentration dependence as well layer distance dependence in the following Chapters. Furthermore, the characterisation techniques and the data analysis are presented for revealing the physics of the energy transfer process.

Chapter 4

Energy Transfer from Quantum Dots to Au Nanoparticles

Due to the unique optical properties of quantum dots (QDs) and colloidal Au nanoparticles (NPs) as mentioned in Sect. 2.1 and 2.3 in Chapter 2, QD-Au NP can be an excellent energy transfer donor-acceptor pair. The distance dependence of the emitter from the Au NPs creates the basis of the nanosensor [26–28] or nanoruler [31, 32]. A good understanding of the distance dependence as well as Au NP concentration dependence is desirable as they are key for good design of the nanoruler or nanosensor with high sensitivity. Thus in this Chapter, we will systematically investigate energy transfer in the QD-Au NP system, Au NP with diameter of $d = 5.5$ nm is selected due to its negligible scattering which is only behaves as a quencher. The LSP absorption peak of Au NP layer centres at ~ 532 nm (See Fig 4.1). Five different sizes of CdTe QDs are selected with emission wavelengths tuned by size only from on resonance to off resonance with respect to the LSP peak of the Au NP layer. QDs emission, Au NP layer absorption as well as sample geometry can be found in Fig 4.1. QD with emission wavelength, $\lambda_{em} = 534$ nm is named as QD-1, $\lambda_{em} = 547$ nm as QD-2, $\lambda_{em} = 559$ nm as QD-3, $\lambda_{em} = 623$ nm as QD-4 and $\lambda_{em} = 660$ nm as QD-5 respectively. The optical properties of all the QD solutions can be found in Appendix A.

4.1 Energy Transfer Signatures

The QD monolayer and QD-Au bilayer are prepared by the layer-by-layer approach, where QD concentrations are similar to exclude the QD concentration dependence of decay lifetime of QD monolayer [127]. The emission spectra and normalised decay curves of QD-5 monolayer, QD-5-Au NP bilayers with varying spacer thickness t are shown in Fig 4.2 (a),

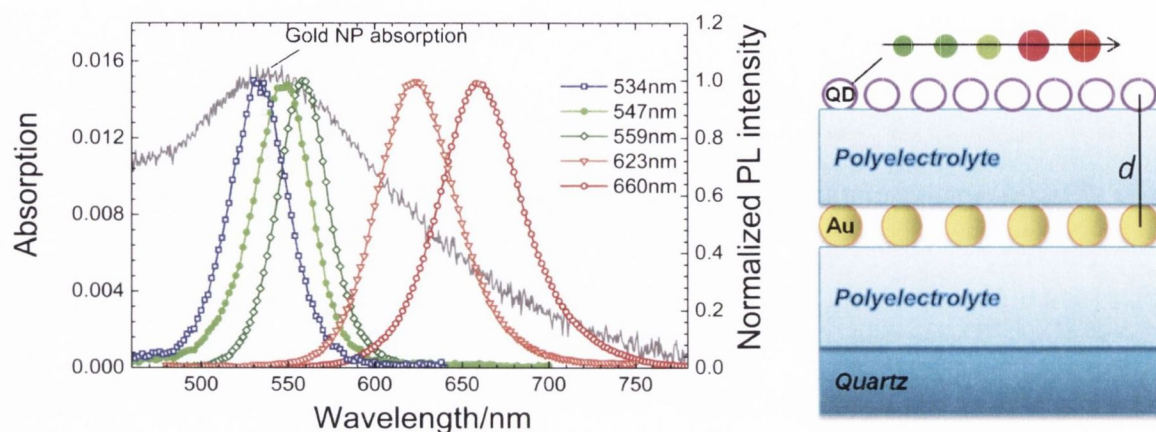


Fig. 4.1 Photoluminescence (PL) spectra of monolayers of each of the five different sizes thioglycolic acid (TGA) stabilised CdTe QDs (right axis), and the absorption spectrum (left axis) of a Au NP layer, with a concentration of $C_{Au} = 0.11 \times 10^{17} \text{m}^{-2}$, (grey line). A schematic of the bilayer structure is also shown.

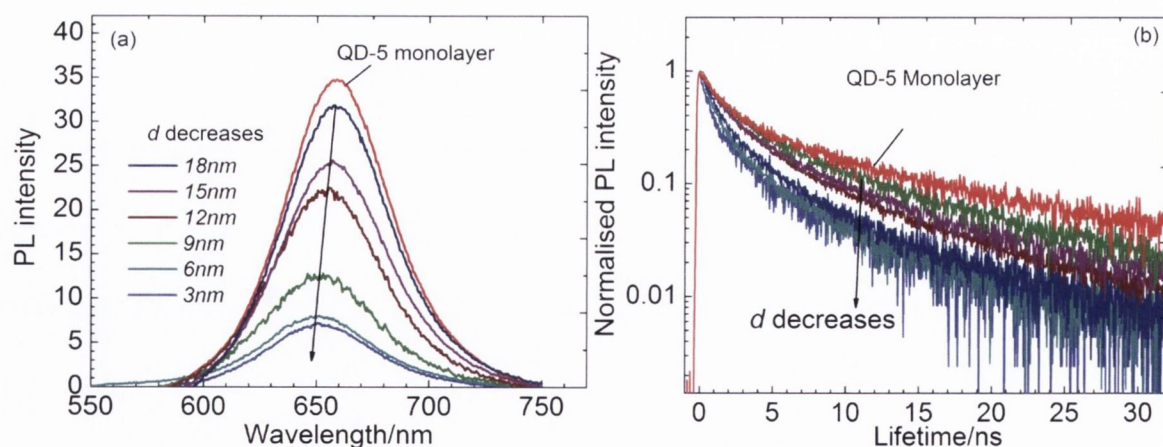


Fig. 4.2 (a) The emission spectra as well as (b) decay curves of QD-5 in the absence and presence of Au NPs with varying spacer thickness, t , the Au NP concentration is kept as $C_{Au} = (0.26 \pm 0.04) \times 10^{17} \text{m}^{-2}$.

(b) respectively. The polyelectrolyte (PE) spacer layer thickness, verified using a X-ray diffraction technique [189], was varied from 3 nm to 18 nm. The details of the PE thickness is discussed in Sect. 3.1.2, Chapter 3. It is clear that emission quenching as well lifetime shortening are observed, which shows dependence on spacer layer thickness or QD-Au NP layer distance. The QD emission quenching effect is strongest at the smallest spacer thickness $t = 3$ nm, and becomes weaker when QD monolayer is positioned further away from Au NP monolayer. The emission of QD-Au NP bilayer shows blue shift with respect to the QD monolayer. Similarly, the decay lifetime of QD monolayer is shortest at $t = 3$ nm while becomes longer with increasing QD-Au NP layer distance.

To quantify the quenching effect by Au NPs, the quenching efficiency can be described by the integrated emission spectra as $Q_{LT} = 1 - \frac{I_{onAu}}{I_{QD}}$, where I_{QD} is the integrated spectral emission of the QD reference monolayer, I_{onAu} is that of the layers deposited on top of Au NP layers. Or the quenching efficiency can be calculated as $Q_{LT} = 1 - \frac{\tau_{onAu}}{\tau_{QD}}$, where τ_{QD} is the PL decay time of the QD reference monolayer, τ_{onAu} is the decay lifetime of QD in the QD-Au NP bilayer.

The emission spectra as well as normalised decay curves of QD reference monolayer and QD-Au bilayer with varying QD-Au NP distance can be found in Fig 4.2 (a) (b), which show dependence on layer distance. it is quenched more when the QD monolayer is positioned closer to Au NP layer.

4.2 Theoretical Formalism

The different formalisms, which are Förster resonance energy transfer (FRET) and nanometal surface energy transfer (NSET), have been reported to describe nonradiative energy transfer for single emitter-metal NP pairs [30, 147]. The basics of both formalisms can be found in Sect. 3.2.1 and Sect. 3.3.1 in Chapter 3 respectively. Here we present the formalisms relevant to energy transfer to a single NP to derive the energy transfer formalisms to a plane of metal NPs.

The nonradiative energy transfer efficiency is given by

$$E = \frac{k_{ET}}{k_{ET} + k_r + k_{nr}} \quad (4.1)$$

where k_r , k_{nr} and k_{ET} are the radiative recombination rate, the nonradiative recombination rate, and the nonradiative energy transfer rate, respectively.

Within the FRET formalism, the QD and Au NP are approximated as point dipoles

[116], and for a single QD-Au NP pair the energy transfer rate can be expressed as

$$k_{\text{FRET}} = \frac{1}{\tau_D} \cdot \left(\frac{R_0}{d} \right)^6 \quad (4.2)$$

where $\tau_D = (\tau_r + \tau_{nr})^{-1}$ is the intrinsic lifetime of the QD emission decay, that can be determined from time-resolved photoluminescence measurements, d is the centre-to-centre distance between the QD and Au NP. R_0 , the Förster radius, is the characteristic distance at which the energy transfer efficiency is 50%, given by [116],

$$R_0 = 0.0211 \left[\frac{\kappa^2 \Phi_{QD} J(\lambda)}{n^4} \right]^{\frac{1}{6}} \quad (4.3)$$

where κ^2 is an orientation factor between the donor and acceptor, $\kappa^2 = 2/3$ is used for a randomly distributed system. Φ_{QD} is the PL quantum yield of the QDs, n is the refractive index of the surrounding medium. J is the spectral overlap of the area-normalised donor QD emission spectrum $\hat{f}_D(\lambda)$ and acceptor Au NP extinction ϵ_{Au} . The QYs of all QDs can be found in Table. 1. The details about the QY calculation can be found in Sect. 3.2.2 while Au NP extinction can be seen in Sect. 3.4.1 in Chapter 3.

$$J = \int_0^\infty \hat{f}_D(\lambda) \cdot \epsilon_{Au}(\lambda) \cdot \lambda^4 d\lambda, \quad (4.4)$$

In the case of bilayer structures (Fig 4.3), the rate of energy transfer to Au NP plane is the sum of decay rate to a single Au NP over acceptor Au NP plane as

$$k_{\text{FRET}} = \frac{1}{\tau_D} \cdot \sum_i \left(\frac{R_0}{d_i} \right)^6 \quad (4.5)$$

where d_i is the centre-to-centre distance between donor-Au NP pair as shown in Fig 4.3. Performing an integration over an infinite plane (the details of derivations of k_{FRET} and E_{FRET} for layered structures can be seen in Appendix B), the energy transfer efficiency can be expressed as

$$E_{\text{FRET}} = \frac{1}{1 + \frac{2d^4}{C_{Au} \cdot \pi \cdot R_0^6}} \quad (4.6)$$

where d is the minimum distance of the QDs and Au NPs plane with $d = t + r_{QD} + r_{Au}$ is the distance between the QD monolayer and Au NP monolayer, which includes the spacer layer thickness, t , as well as the radii of the QD, r_{QD} and Au NP, r_{Au} as seen in Fig 4.3. C_{Au} is the Au NP concentration.

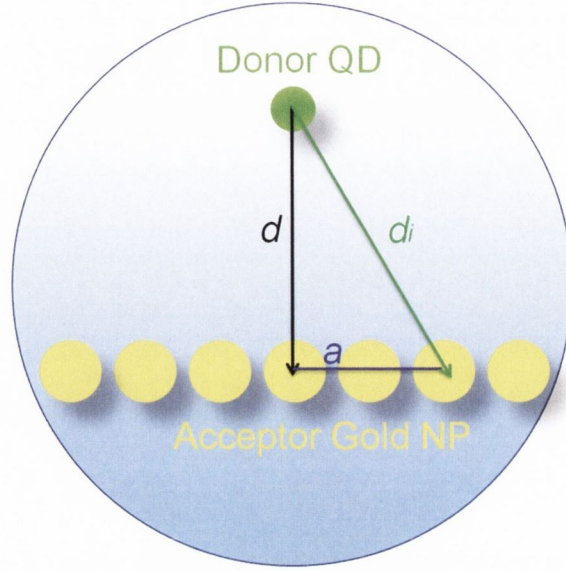


Fig. 4.3 Cartoon of donor dipole interaction with a layer of acceptor Au NPs where a Au NP is regarded as a dipole or a nano surface, If a Au NP is treated as a dipole, the QD-Au distance is described as d_i , the minimum QD-Au distance is $d = t + r_{QD} + r_{Au}$; if a Au NP is treated as a nano surface, the QD-Au distance is $d_i - r_{Au}$ and the minimum QD-Au distance is $d - r_{Au}$.

Within the NSET formalism, energy transfer for a single QD-Au NP pair is considered to occur from a donor point dipole QD to an infinite Au surface [157]. The energy transfer rate to a single Au NP can be expressed [29, 31] as

$$k_{\text{NSET}} = \frac{1}{\tau_D} \cdot \left(\frac{d_0}{d_i - r_{Au}} \right)^4 \quad (4.7)$$

where the distance between the QD and the Au surface includes only the QD radius and the spacer layer thickness, t , which is $d_i - r_{Au}$ (see Fig 4.3). The characteristic distance for which the NSET efficiency is 50%, denoted as d_0 , can be calculated from

$$d_0 = 0.225 \left[\frac{\Phi_{QD} \cdot c^3}{w_{QD}^2 \cdot w_F \cdot k_F \cdot n} \right]^{\frac{1}{4}} \quad (4.8)$$

where $w_F = 8.4 \times 10^{15}$ rad/s and $k_F = 1.2 \times 10^8$ cm⁻¹ are the bulk Au angular frequency and Fermi vector, respectively, c is the speed of light [29], and w_{QD} is the QD emission frequency. n is the refractive index of the medium, which is absent in Ref [29, 31]. The inclusion of the refractive index in this manner is justified by observing that the radiative decay rate in a medium of refractive index n is given by $k_r = nk_r^0$, where k_r^0 is the radiative

decay rate in vacuum.

In case of bilayer structures, with each QD-Au NP pair interaction treated within the NSET formalism, the rate of energy transfer to the Au NP plane is expressed as

$$k_{\text{NSET}} = \frac{1}{\tau_{\text{D}}} \sum_i \left(\frac{d_0}{d_i - r_{\text{Au}}} \right)^4 \quad (4.9)$$

By integration over Au NP plane, E_{NSET} can be expressed as

$$E_{\text{NSET}} = \left[1 + \frac{3(d - r_{\text{Au}})^3}{C_{\text{Au}} \pi d_0^4 (3d - r_{\text{Au}})} \right]^{-1} \quad (4.10)$$

The details of derivations of k_{NSET} and E_{NSET} for layered structures can be found in Appendix B. The nonradiative energy transfer efficiency for a QD interacting with a plane of Au NP acceptors within the NSET formalism shows a d^{-2} distance dependence as opposed to the d^{-4} dependence for FRET to a plane of acceptors.

4.3 Distance Dependence

The distance dependent quenching, as a function of the PE spacer layer thickness, is shown for four QDs in Fig 4.4 (a)-(d). The Au NP concentration was adjusted slightly to achieve a similar quenching range for the different QDs. The Au NP concentration dependence of the quenching efficiency is fully examined in the next section. For all QDs the PL emission quenching increases as the distance between the QD and Au NP monolayers is reduced, and the lifetime shortens more as the QD monolayer is brought in closer proximity to the Au NP layer. Firstly, it can be noted that there is close agreement of the PL quenching with the lifetime quenching indicating that the change in the QD PL and lifetime is due only to changes in the nonradiative rate, through the introduction of the additional mechanism of energy transfer to the Au NPs, and that the QD radiative rate, k_r , is unchanged [190]. It is also expected that the intrinsic non-radiative rate, k_{nr} , of the QD is unaffected by the QD-Au NP interaction [156]. Therefore, the PL and lifetime quenching are signatures of the nonradiative energy transfer mechanism from the QD to the Au NP layer and the energy transfer efficiency is $E = Q_{\text{PL}} = Q_{\text{LT}}$.

The distance dependence can firstly be analysed within the FRET model. The experimental FRET efficiency can be fitted using eq 4.6. As the centre-to-centre distance, d , and the Au NP concentration, C_{Au} , have been independently measured, the Förster radius, R_0 , can be determined from the fit. The best fit is shown as solid black line on each of the

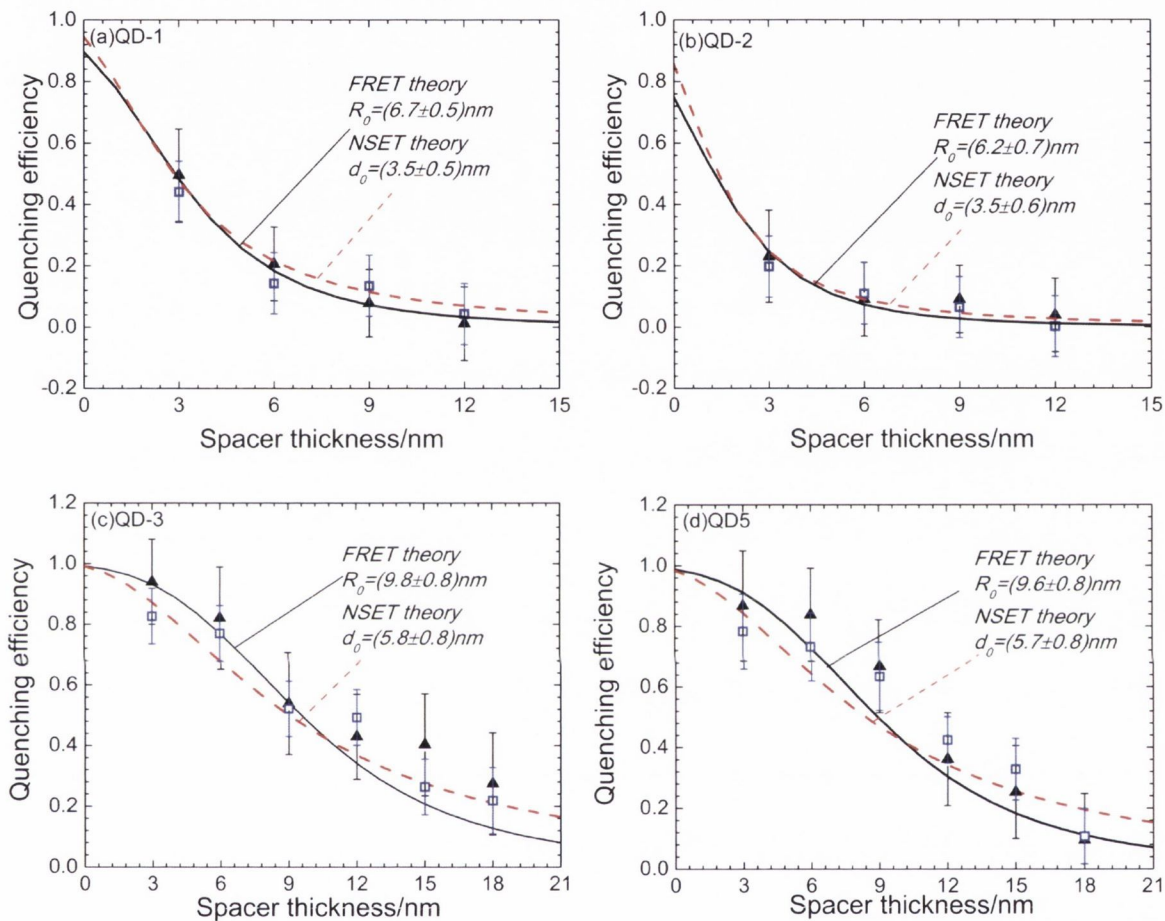


Fig. 4.4 Distance dependence of the quenching efficiency, E , of QD monolayers deposited on top of a Au NP monolayer. The PL quenching efficiency was determined from the integrated PL spectra for the overall ensemble emission (solid black triangle) and the lifetime quenching was determined from the average decay lifetimes (open blue square). The solid line (black) represents the fit of the quenching efficiency with a model based on the FRET mechanism. The dashed line (red) represents the fit of the quenching efficiency with a model based on the NSET mechanism. (a) QD-1 $\lambda_{em} = 534 \text{ nm}$, $C_{Au} = (0.16 \pm 0.01) \times 10^{17} \text{ m}^{-2}$, (b) QD-2 $\lambda_{em} = 547 \text{ nm}$, $C_{Au} = (0.09 \pm 0.01) \times 10^{17} \text{ m}^{-2}$, (c) QD-3 $\lambda_{em} = 559 \text{ nm}$, $C_{Au} = (0.21 \pm 0.03) \times 10^{17} \text{ m}^{-2}$, (d) QD-5 $\lambda_{em} = 660 \text{ nm}$, $C_{Au} = (0.26 \pm 0.04) \times 10^{17} \text{ m}^{-2}$.

Table 4.1 **Properties of the QDs: central emission wavelength (nm), diameter (nm) and QY of the QD monolayers on quartz.** The calculated R_0 is determined from eq 4.3 using the spectral overlap, J , and quantum yield, QY . The calculated d_0 is determined from eq 4.8 using the central emission wavelength and quantum yield, QY . The experimental R_0 and d_0 are the averages of the values obtained from fitting the distance and Au NP concentration dependences shown in Fig 4.4 and Fig 4.5.

QD	QD1	QD2	QD3	QD4	QD5
central emission wavelength (nm)	534	547	559	623	660
QD diameter (nm)	2.55	2.6	2.7	3.3	3.4
Quantum Yield, QY	3.5%	3.5%	6%	11%	6%
spectral overlap, J (nm ⁴ /(M · cm))	2.55×10^{17}	2.6×10^{17}	2.7×10^{17}	3.3×10^{17}	3.4×10^{17}
calculated R_0 (nm)	(6.9 ± 0.5)	(6.7 ± 0.5)	(7.5 ± 0.5)	(8.0 ± 0.5)	(7.5 ± 0.5)
experimental R_0 (nm)	(6.7 ± 0.6)	(6.2 ± 0.6)	(9.4 ± 0.8)	(9.9 ± 0.7)	(9.5 ± 0.8)
calculated d_0 (nm)	(3.3 ± 0.4)	(3.4 ± 0.4)	(3.8 ± 0.5)	(4.7 ± 0.5)	(4.2 ± 0.5)
experimental d_0 (nm)	(3.7 ± 0.6)	(3.5 ± 0.6)	(5.7 ± 0.8)	(5.7 ± 0.7)	(5.5 ± 0.8)

graphs in Fig 4.4, and the extracted Förster radii, R_0 , are given on each graph. Firstly, it can be noted that the trend of the experimental data can be well predicted by the form of eq 4.6. Secondly, Förster radii greater than 6 nm are observed in all cases. These are relatively large values compared to the Förster radii determined for FRET between donor and acceptor QDs for solid-state structures at room temperature [124, 127, 189], but similar to the characteristic interaction distances reported for energy transfer from QDs to 1.4 nm Au NPs [30]. It can also be noted that the measured Förster radius is larger for the off-resonance QDs, red-shifted from the localized surface plasmon resonance. This would suggest that the Au NP-QD interaction is stronger for QDs red shifted with respect to the localised surface plasmon resonance rather than in resonance.

4.4 Au NP Concentration Dependence

The Au NP concentration dependence of the PL and lifetime quenching is shown in Fig 4.5 (a)-(e). The Au NP concentration was varied from approximately $C_{Au} = 0.05 \times 10^{17} \text{m}^{-2}$ to $C_{Au} = 0.35 \times 10^{17} \text{m}^{-2}$. The PE spacer layer thickness, t , is indicated on each plot. As the strength of QD-Au NP interaction varies for the different QD species, the spacer layer thickness was adjusted to have similar quenching efficiencies for all five QDs over the concentration range. Again, there is close agreement of the PL and lifetime quenching data, as was observed for the distance dependent data. The Förster radius for each QD-Au NP pair can be extracted by fitting with eq 4.6. The centre-to-centre distance, d , is known for each

pair. The best fit is shown as the solid black line on each of the plots in Fig 4.5, and the extracted Förster radii, R_0 , are also given on each graph. Firstly, similar to what was observed for the distance dependence of the energy transfer efficiency, the trend of the experimental data is in good agreement with the FRET model, and secondly, there is close agreement between the Förster radii determined from the concentration and distance dependences for QD-1, QD-2, QD-3 and QD-5. The average R_0 value for each QD is given in Table 1. To provide an additional data point for the wavelength dependence of the quenching, the Au concentration dependence for QD-4, with central emission wavelength at 623 nm, has also been shown in Fig 4.5 and the R_0 extracted from the fit is included in Table 1.

4.5 Spectral Analysis

Using eq 4.3, R_0 can be estimated from the spectral overlap of the area-normalised donor (QD) emission spectrum, $\hat{f}_D(\lambda)$, and the acceptor (LSP) extinction spectrum, $\epsilon_{Au}(\lambda)$ from eq 4.4 and 4.3. The spectral overlap and QY for the QD monolayers is also given in Table 1 and the volume weighted refractive index is $n = (1.5 \pm 0.3)$. The calculated R_0 values can be compared with those obtained from fitting the distance and Au NP concentration dependence. The calculated R_0 shows a relatively small variation of approximately 1nm over the full wavelength range. It is seen that for the QD-1 and QD-2, emitting close to the localised surface plasmon resonance, there is reasonable agreement between the values obtained from the fitting and those calculated from spectral overlap. However, for QD-3, QD-4 and QD-5, with emission red-shifted from the localised surface plasmon resonance, the values obtained from the fitting the distance and Au NP concentration dependences are significantly larger than those calculated from the spectral overlap. Therefore, analysis of the QD emission quenching within the FRET formalism does not provide good agreement between experiment and theory over the full wavelength range. Additionally, as mentioned earlier, the larger R_0 values imply that LSP-QD interaction, and consequently energy transfer from QDs to the Au NPs, is more efficient when the QD emission is red-shifted off the localised surface plasmon resonance, contrary to expectations. This stronger interaction is also reflected in the increased distance between the off-resonance QD monolayers and the Au NP monolayer to obtain a similar level of quenching as for the on-resonance QD bilayer samples. While the trends of the experimental data could be well reproduced by FRET theory, the characteristic interaction distance obtained from fitting the experimental data with theory does not agree with the value calculated from the spectral overlap over the full wavelength range. Therefore, NSET theory was considered as an alternative model to explain the

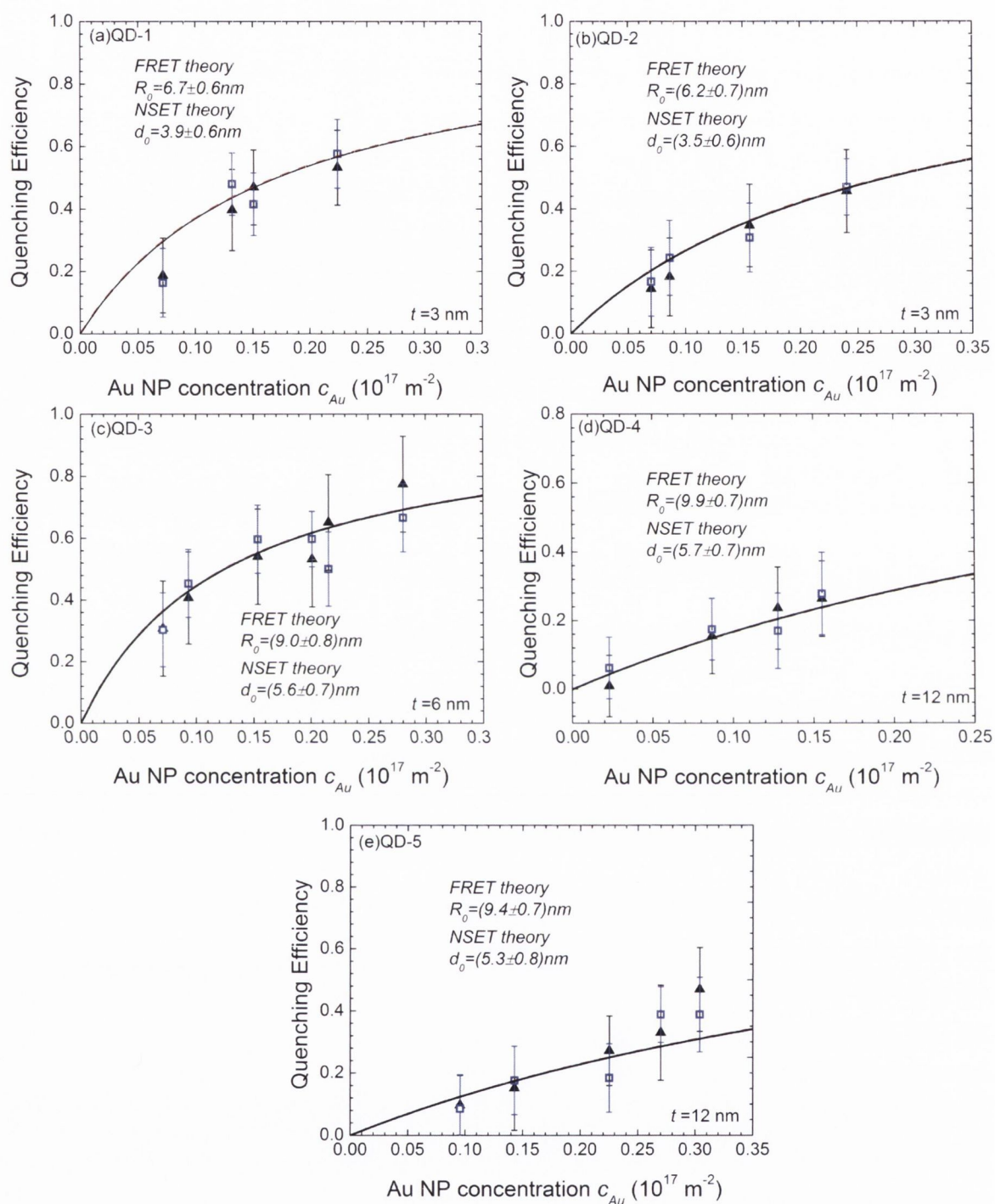


Fig. 4.5 Au NP concentration dependence of the quenching efficiency, E , of QD monolayers deposited on top of a Au NP monolayer. The PL quenching efficiency was determined from the integrated PL spectra for the overall ensemble emission (solid black triangle) and the lifetime quenching was determined from the average decay lifetimes (open blue square). The solid line (black) represents the fit of the quenching efficiency with a model based on the FRET mechanism. The fit of the quenching efficiency with a model based on the NSET mechanism overlaps the fit from the FRET model. (a) QD-1 $\lambda_{em} = 534 \text{ nm}$, (b) QD-2 $\lambda_{em} = 547 \text{ nm}$, (c) QD-3 $\lambda_{em} = 559 \text{ nm}$, (d) QD-4 $\lambda_{em} = 623 \text{ nm}$, (e) QD-5 $\lambda_{em} = 660 \text{ nm}$.

distance and concentration dependences of the quenching efficiency.

4.6 NSET Analysis

To investigate the NSET mechanism for energy transfer to a plane of Au NPs, the distance and Au NP concentration data can be fitted using eq 4.10 with d_0 as the fit parameter. All other parameters have been independently measured, and in this case the relevant distance is from the centre of the QD to the Au NP surface, $d - r_{Au}$. The best fits are shown as dashed lines in Fig 4.4 and Fig 4.5. The corresponding d_0 values are given on each graph. The dependence of E_{NSET} on the spacer layer thickness is clearly different to that of E_{FRET} ; however a good fit to the experimental data, within the measurement error, can be observed for all four QD species shown in Fig 4.4. As can be clearly seen from eq 4.6 and eq 4.10, E_{NSET} has the same Au NP concentration dependence as E_{FRET} and therefore, the fits overlay each other in Fig 4.5. There is good agreement between the d_0 values extracted from the distance and Au NP concentration dependences, and the average values for each QD are given in Table 1.

The d_0 values extracted from the fitting can be compared with those calculated using eq 4.8. The QD emission frequency is calculated using the central emission wavelength and QD monolayer QY, given in Table 1. The calculated d_0 values for each of the five QDs are also given in Table 1. It can be seen that the fitted and calculated values are in closer agreement across the entire wavelength range than is found using FRET analysis. In particular, the values for QD-1 and QD-2, emitting close the localised surface plasmon peak, agree within the experimental error.

At this point it can be noted that we have not considered the Au monolayer itself as an infinite surface, in which case the energy transfer rate would be given by eq 4.7 and the surface energy transfer efficiency would be described by $E = \frac{1}{1 + \left(\frac{d-r_{Au}}{d_0}\right)^4}$. Such an approach would neglect the observed strong Au NP concentration dependence observed in the bilayer structures. Instead, this is the form of the NSET transfer efficiency for a single emitter-Au NP pair [29]. However, it is worth commenting that the d_0 values obtained by fitting the distance and concentration dependent data with this expression also show a large discrepancy with the calculated values for the three off-resonance QDs, similar to what was observed using the FRET analysis.

4.7 Conclusion

In conclusion, five different sized CdTe QDs have been used to probe the wavelength dependence of quenching of a QD monolayer deposited in proximity to a plane of 5.5 nm diameter Au NPs. Strong QD emission quenching is observed for QDs red-shifted by 120 nm from the peak of the LSP resonance. We have shown that while the distance and Au NP concentration dependences of the quenching efficiencies for all five QDs follow trends that can be fitted with a model for FRET between two planes, the extracted Förster radii do not agree with expected values for QDs emitting off the LSP resonance. Agreement within experimental error is only observed for QDs emitting close to the LSP peak. Analysis using a NSET model for the QD-Au NP interaction can also predict the trends of the distance and Au NP concentration dependences of the nonradiative energy transfer. It is found that closer agreement between the extracted characteristic distance, d_0 , and the theoretically expected value is observed over the full wavelength range. While further theoretical studies are required to explain the approximation of metal NPs of such small dimensions as infinite surfaces within NSET approach, this experimental study suggests that the NSET formalism can be a convenient phenomenological tool for the analysis of emission quenching due to nonradiative energy transfer to a plane of metal NPs.

Chapter 5

Localised Surface Plasmon Coupled Energy Transfer in Quantum Dots

It has been theoretically proposed that localised surface plasmon (LSP) supported by metal nanoparticles (NPs) can modify Förster resonance energy transfer (FRET) [52–54]. Several experiments have verified this phenomenon [51, 57, 59–64, 191]. FRET has wide applications in light emitting diodes [15, 73], sensors [192] and energy harvesting geometries [13, 193]. Therefore, LSP provides an alternative to improve FRET efficiency or extend the FRET ranges to enable the better applications. However, LSP coupled FRET is complex not only due to various parameter dependences, such as separation, optical properties of FRET pairs (spectral overlap, quantum yield), but also the interaction of LSP and donor/acceptor separately [63]. In some cases, LSP even switches off FRET [67]. It is important to understand how LSP coupled FRET parameters, such as energy transfer efficiency, rate, and characteristic distance, depend on the separation between the donor and acceptor in the presence of plasmonic structures.

In this chapter, trilayer structures, which compose of an intermediate Au NP layer between donor QD monolayer and acceptor QD monolayer, are adopted as it has been theoretically proposed as the most efficient geometry for LSP coupled FRET [54]. The trilayers with varying separations between the constituent layers and varying gold NP concentrations are fully characterised to determine how coupling to plasmonic nanostructures influences the distance dependence of LSP coupled FRET. Experimental measurements show evidence of strong donor-plasmon coupling and a dipole-dipole FRET-like distance dependence of the LSP coupled FRET is observed. It is found that the extended energy transfer range, in comparison with conventional FRET, can be described by an increase in the effective Förster radius in the presence of metal NPs. A theoretical study was undertaken by Dr. Cristian A.

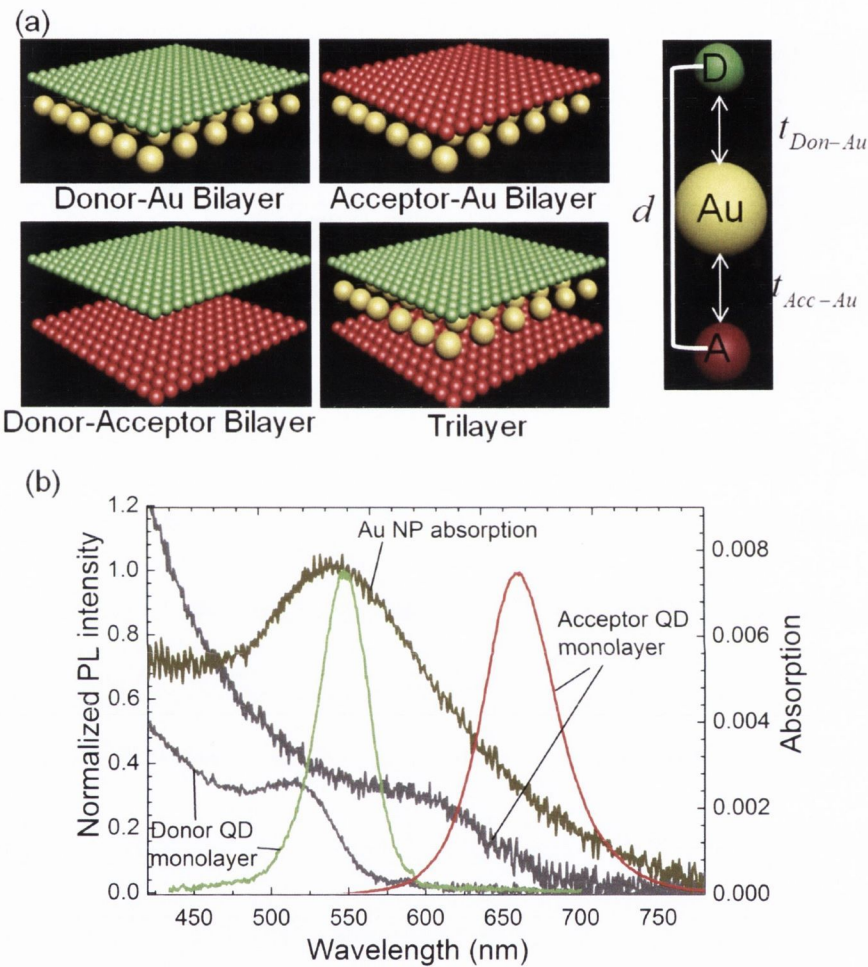


Fig. 5.1 (a) Schematics of the trilayer, donor-acceptor bilayer and QD-Au NP bilayer reference structures. The PE spacer layer thickness is denoted by t , where t_{Don-Au} , t_{Acc-Au} correspond to the PE spacer layer thickness between the intermediate Au NP monolayer and the donor QD monolayer, Au NP monolayer and acceptor QD monolayer, respectively. The donor-acceptor centre-to-centre distance is denoted by d . (b) Normalized PL spectra of a donor QD monolayer (green line) and acceptor QD monolayer (red line). Absorption spectra of both QD monolayers and Au NP layer are also shown.

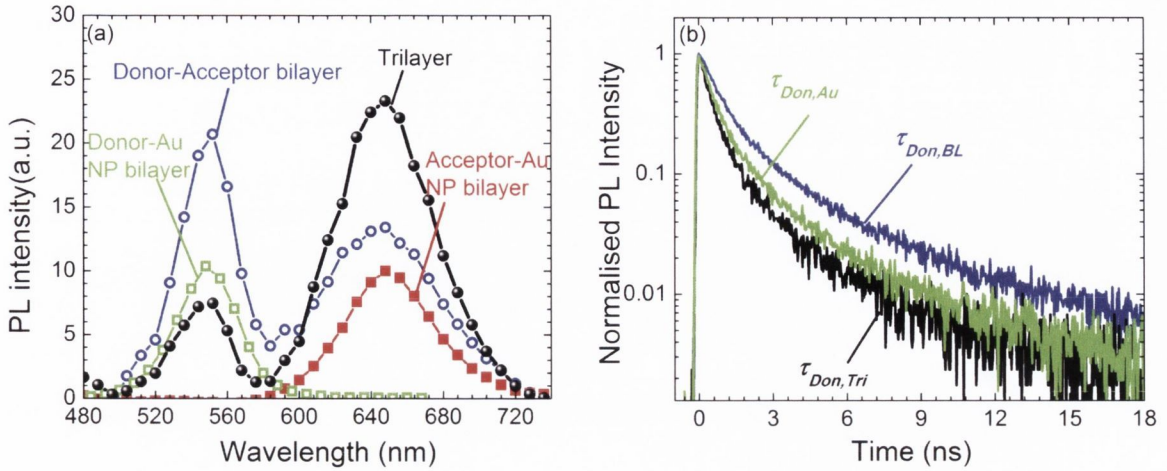


Fig. 5.2 (a) PL spectra of the donor-acceptor bilayer with a $t_{Don-Acc} = 21$ nm (blue open circle), donor-Au NP bilayer with $t_{Don-Au} = 3$ nm (green open square), acceptor-Au NP bilayer with $t_{Acc-Au} = 12$ nm (red filled squares), acceptor-Au NP-donor trilayer structure (black line, black spheres), schematics can be seen in Fig 5.1 (a). All samples have $C_{Don} = (2.8 \pm 0.2) \times 10^{17} \text{m}^{-2}$ and $C_{Acc} = (0.48 \pm 0.08) \times 10^{17} \text{m}^{-2}$, respectively. The Au NP concentration is $C_{Au} = (0.13 \pm 0.03) \times 10^{17} \text{m}^{-2}$. (b) Normalized donor PL decays (550 nm filter) for the donor-acceptor bilayer, labeled $\tau_{Don,BL}$, donor-Au NP bilayer with $t_{Don-Au} = 3$ nm, labeled $\tau_{Don,Au}$, and the trilayer, labeled $\tau_{Don,Tri}$.

Marocico to further investigate the ranges over which the FRET-like distance dependence of the LSP coupled FRET mechanism is valid for this experimental system. The theoretical results also demonstrate that greater enhancement of the LSP coupled FRET efficiency is achieved for preferential donor-plasmon coupling compared with acceptor-plasmon coupling. These theoretical results provide complementary insight into the experimental results and a discussion of the theoretical results is presented for completeness.

5.1 Signatures of Localised Surface Plasmon Coupled Energy Transfer

Multilayer planar structures in this chapter are prepared with QD-1 and QD-5 (see Appendix A) solutions and colloidal Au NP solutions (see Sect. 3.4, Chapter 3). The trilayer structure is composed of an acceptor QD monolayer, an intermediate Au NP monolayer, and a donor QD monolayer, each separated by a PE spacer layer. Donor-acceptor QD bilayer, QD-Au NP bilayer are also built as reference samples. Schematics of all structures are shown in Fig 5.1 (a).

The donor QDs, with a diameter of 2.6 nm, have an emission peak at 547 nm in layer.

The larger acceptor QDs, with a diameter of 3.4 nm, have maximum emission at 660 nm in layer. Emission and absorption spectra for the donor and acceptor QD and Au NP monolayers are shown in Fig 5.1(b). As can be seen, this donor-acceptor QD pair has spectrally separated PL emission spectra. For measurement of the PL decays a broadband filter centred at 550 nm or 650 nm with a FWHM of approximately (70 ± 5) nm were used to record the donor or acceptor emission. Colloidal Au NPs have diameter of 5.5 nm. The Au NP and QD monolayer concentrations were determined from the absorption spectra [159, 171, 187], details can be found in Chapter 3. The LSP resonance of the Au NP monolayer is clearly evident from the peak in the absorption spectrum at ~ 532 nm, which overlaps well with the donor emission peak, see Fig 5.1 (b).

Fig 5.2 (a) shows the PL spectra of the trilayer structure as well as reference donor-acceptor QD and QD-Au NP bilayer samples. The trilayer sample has $t_{Don-Au} = 3$ nm and $t_{Acc-Au} = 12$ nm. The donor and acceptor QD monolayers in the reference bilayer sample are separated by a PE spacer layer with thickness $t_{Acc-Don} = 21$ nm, which is equivalent to the surface-to-surface donor-acceptor separation in the trilayer structure. The samples have similar donor and acceptor QD concentrations, $C_{Don} = (2.8 \pm 0.2) \times 10^{17} \text{ m}^{-2}$ and $C_{Acc} = (0.52 \pm 0.04) \times 10^{17} \text{ m}^{-2}$, respectively. The Au NP concentration is $C_{Au} = (0.15 \pm 0.02) \times 10^{17} \text{ m}^{-2}$. As can be seen in Fig 5.2 (a), the acceptor emission in the trilayer sample is increased compared to the Au-absent donor-acceptor bilayer reference sample. The spectrum shows enhancement of the acceptor emission by a factor $\eta = \frac{I_{Acc,Tri}}{I_{Acc,BL}} = 2.2$, where $I_{Acc,Tri}$ and $I_{Acc,BL}$ are the integrated acceptor PL in the trilayer structure and donor-acceptor bilayer reference sample, respectively. The donor and acceptor QD-Au NP bilayer structures show reduced emission relative to the donor-acceptor bilayer which is a consequence of the PL quenching effect of the 5.5 nm diameter Au NP layer as discussed in Chapter 4. The PL quenching arises due to direct nonradiative energy transfer from the QDs to the Au NPs [194]. Therefore, the large acceptor emission enhancement in the trilayer structure is attributed to LSP coupled FRET from the donor to acceptor QDs.

The normalised PL decay curves of donor are shown in Fig 5.2 (b). The donor PL decay shows a reduction of the average lifetime in the donor-Au NP bilayer structure, $\tau_{Don-Au} = (2.8 \pm 0.2)$ ns, compared to the reference donor-acceptor bilayer structure, $\tau_{Don-BL} = (3.7 \pm 0.2)$ ns. In the trilayer structure, the donor lifetime is further shortened to $\tau_{Don-Tri} = (2.24 \pm 0.06)$ ns due to the introduction of the LSP coupled FRET mechanism from the donor QDs to the acceptor QDs. The LSP coupled FRET efficiency can be calculated as $E_{LSP-FRET} = 1 - \frac{\tau_{Don,Tri}}{\tau_{Don,Au}} = 20\%$ while the LSP coupled FRET rate can be calculated as $k_{LSP-FRET} = \tau_{Don,Tri}^{-1} - \tau_{Don,Au}^{-1} = 0.09 \text{ ns}^{-1}$ for the example shown in Fig 5.2 (b).

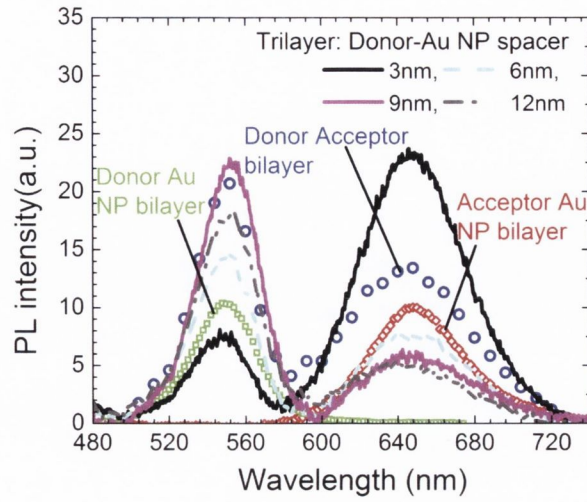


Fig. 5.3 The PL spectra and of the donor-acceptor bilayer with a $t_{Don-Acc} = 21$ nm (blue open circle), donor-Au NP bilayer with $t_{Don-Au} = 3$ nm (green open square) and the acceptor-Au NP bilayer with $t_{Acc-Au} = 12$ nm (red open diamond) which is subsequently capped with a PE spacer layer, $t_{Don-Au} = 3$ nm, and the donor QD monolayer to form the completed trilayer structure (black line). Spectra with varying donor-Au spacer are shown with a fixed acceptor-Au NP spacer layer thickness, $t_{Acc-Au} = 12$ nm. All samples have $C_{Don} = (2.8 \pm 0.2) \times 10^{17} \text{m}^{-2}$ and $C_{Acc} = (0.48 \pm 0.08) \times 10^{17} \text{m}^{-2}$, respectively. The Au NP concentration is $C_{Au} = (0.13 \pm 0.03) \times 10^{17} \text{m}^{-2}$.

5.2 Donor-Au NP Separation Dependence

To examine the dependence of the LSP coupled FRET signatures on the position of the Au NP monolayer, two distance dependent studies were undertaken. In the first case the acceptor QD-Au NP spacer layer thickness, t_{Acc-Au} , is constant while the donor QD-Au NP spacer layer thickness, t_{Don-Au} , is varied. In the second case, t_{Don-Au} is fixed with varying t_{Acc-Au} , which will be shown in next section.

Fig 5.3 shows the PL spectra of donor-acceptor reference as well as trilayer samples with fixed $t_{Acc-Au} = 3$ nm while t_{Don-Au} varying from 3 nm to 12 nm. All samples have similar concentrations as $C_{Don} = (2.8 \pm 0.2) \times 10^{17} \text{m}^{-2}$, $C_{Acc} = (0.48 \pm 0.08) \times 10^{17} \text{m}^{-2}$, and $C_{Au} = (0.13 \pm 0.03) \times 10^{17} \text{m}^{-2}$, respectively. It was observed that the donor PL increases with increasing donor-Au NP separation, which is expected due to reduced direct quenching of the donor emission by nonradiative energy transfer to the Au NPs. Furthermore, the acceptor PL rapidly reduces attributed to the reduced LSP coupled energy transfer to the acceptors. Enhancement of the acceptor PL is observed only for the smallest donor-Au NP separation, after which the acceptor PL becomes dominated by the direct quenching by the Au NP layer.

The corresponding donor PL decays are shown in Fig 5.4 (a). The decay for t_{Don-Au}

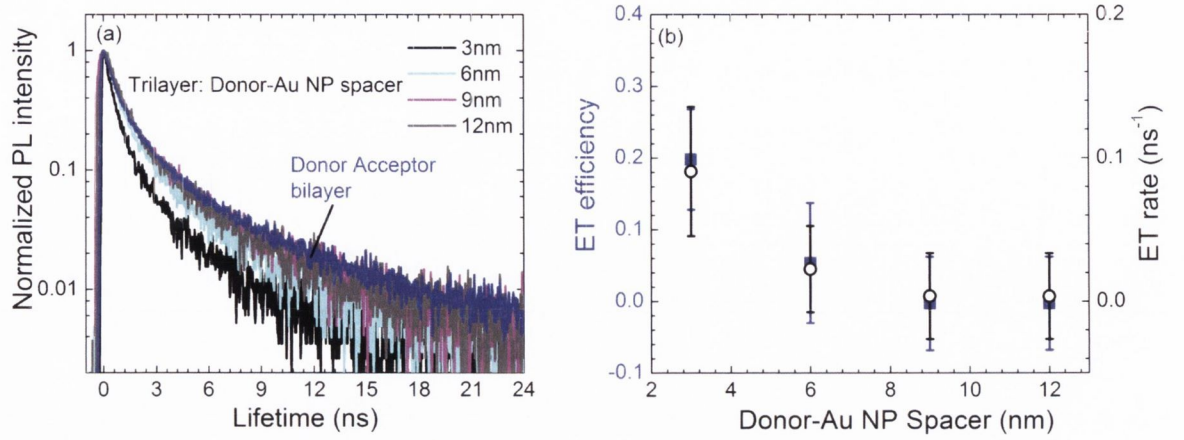


Fig. 5.4 (a) The PL decay curves for the donor-acceptor bilayer reference sample as well as the trilayer samples with varying t_{Don-Au} as shown. (b) The calculated energy transfer efficiency (left-hand axis, blue squares) as well as energy transfer rate (right-hand axis, black circles) as a function of donor-Au spacer thickness.

$= 3$ nm is the shortest, the decay becomes longer with increasing t_{Don-Au} and tend towards the reference bilayer sample. The LSP coupled FRET efficiency, calculated from the donor PL decays as $E_{LSP-FRET} = 1 - \frac{\tau_{Don,Tri}}{\tau_{Don,Au}}$ and the LSP coupled FRET rate, calculated by $k_{LSP-FRET} = \tau_{Don,Tri}^{-1} - \tau_{Don,BL}^{-1}$ are plotted in Fig 5.4 (b). The energy transfer efficiency as well as energy transfer rate decrease to ~ 0 for $t_{Don-Au} = 9$ nm.

5.3 Acceptor-Au NP Separation Dependence

Next we probe the dependence of the LSP coupled FRET efficiency on the acceptor-Au NP separation, t_{Acc-Au} . The donor-Au NP spacer layer thickness, t_{Don-Au} , is fixed at 3 nm, while t_{Acc-Au} is varied from 3 nm to 27 nm. The Au NP concentration is fixed at $C_{Au} = (0.12 \pm 0.01) \times 10^{17} \text{m}^{-2}$, with donor and acceptor QD concentrations of $C_{Don} = (1.8 \pm 0.2) \times 10^{17} \text{m}^{-2}$ and $C_{Au} = (0.8 \pm 0.1) \times 10^{17} \text{m}^{-2}$, respectively.

The donor PL decay lifetimes for the trilayer structures and a donor-Au NP bilayer (with fixed separation of 3 nm and the same Au NP concentration) are used to calculate the LSP coupled FRET efficiency, $E_{LSP-FRET} = 1 - \frac{\tau_{Don,Tri}}{\tau_{Don,Au}}$. Fig 5.5 (a) shows $E_{LSP-FRET}$ as a function of the acceptor-Au NP separation, t_{Acc-Au} , and the donor-acceptor centre-to-centre separation,

$$d = r_{Don} + 3\text{nm} + 2 \times r_{Au} + t_{Acc-Au} + r_{Acc}, \quad (5.1)$$

in which r_{Don} , r_{Acc} and r_{Au} are the donor QD, acceptor QD and Au NP radii, respectively (see Fig 5.1 (a)). An acceptor-Au NP separation, t_{Acc-Au} , ranging from 3 nm to 27 nm corresponds to donor-acceptor centre-to-centre distances, d , varying from 14.5 nm to 38.5 nm. LSP coupled FRET efficiency falls off quickly with increasing donor-acceptor separation as shown in Fig 5.5 (a). For donor-acceptor bilayer where LSP is absent, the FRET efficiency between monolayers of donor and acceptor QDs has been previously shown to be well described by

$$E_{FRET} = \left[1 + \frac{2d^4}{C_{Acc} \cdot \pi \cdot R_0^6}\right]^{-1} \quad (5.2)$$

where d is the centre-to-centre distance, R_0 is the Förster radius, and C_{Acc} is the acceptor QD concentration. $R_0 = 4.2$ nm is calculated from the spectral overlap of the donor QD emission and acceptor QD absorption for this donor-acceptor pair, using a volume weighted refractive index $n = 1.5$ and the measured quantum yield of the donor QD monolayer of 3% [127]. The FRET efficiency for the donor-acceptor bilayers is shown in Fig 5.5 using the same acceptor concentration as for the trilayer system.

The interaction between monolayers of CdTe QDs and 5.5 nm diameter Au NPs has been the subject of a previous separate study in Chapter 4. It was previous shown that the dependence of the nonradiative energy transfer efficiency on both the separation between the QDs and Au NPs, or the Au NP concentration, in a QD-Au NP bilayer structure, could be described using a NSET formalism. The NSET efficiency for energy transfer from the QDs to a plane of metal nanoparticle acceptors is given by (details can be found in Appendix B),

$$E_{NSET} = \left[1 + \frac{3(d - r_{Au})^3}{C_{Au} \cdot \pi \cdot d_0^4 \cdot (3d - r_{Au})}\right]^{-1} \quad (5.3)$$

where d_0 is the characteristic distance at which the energy transfer efficiency is for a single emitter-metal NP pair. In this case the metal NP is the energy acceptor and d is the donor-acceptor centre-to-centre distance between the QD monolayer and Au NP monolayer. E_{NSET} is calculated using a Au NP concentration of $C_{Au} = (0.12 \pm 0.01) \times 10^{17} \text{ m}^{-2}$ and $d_0 = 3.1$ nm (determined from the reference donor-Au NP bilayer samples).

Comparison of the three cases can be seen in Fig 5.5. It shows clearly the large enhancement of the energy transfer range *via* LSP coupled FRET. Using eq 5.2, which is $E_{FRET} = \left[1 + \frac{2d^4}{C_{Acc} \cdot \pi \cdot R_0^6}\right]^{-1}$ to fit the data in Fig 5.5 (a), $R_0 = (8.1 \pm 0.7)$ nm is obtained from the fitting, which which can be considered as the LSP enhanced effective Förster radius. The enhanced R_0 corresponds to an approximately ~ 2 fold increase in the Förster

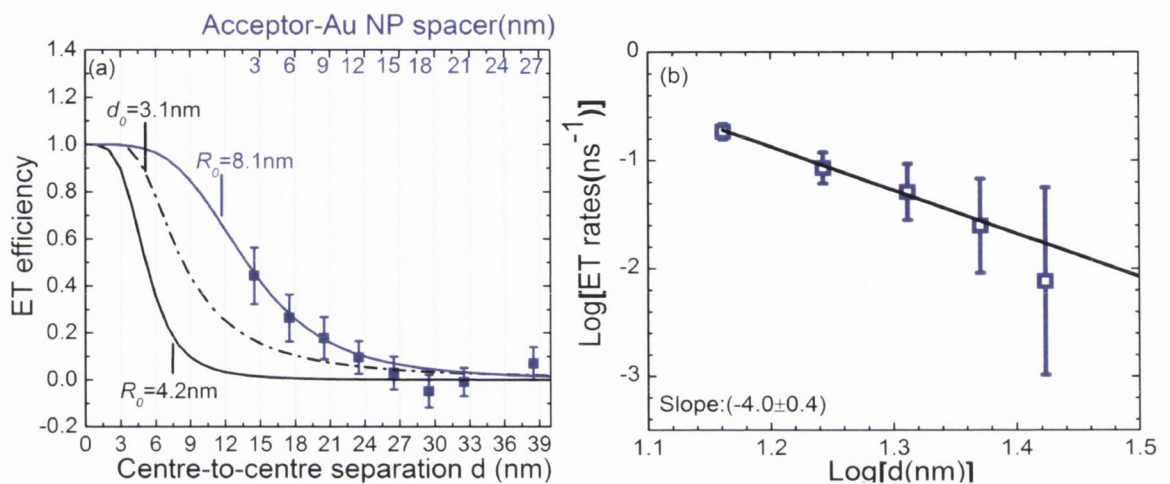


Fig. 5.5 (a) The LSP coupled FRET efficiency in trilayer structures (blue solid squares) with varying acceptor-Au NP spacer thickness, t_{Don-Au} (top axis), and a fixed donor-Au NP spacer thickness, $t_{Don-Au} = 3$ nm. All samples have $C_{Acc} = (0.8 \pm 0.1) \times 10^{17} \text{m}^{-2}$, $C_{Don} = (1.8 \pm 0.2) \times 10^{17} \text{m}^{-2}$ and $C_{Au} = (0.12 \pm 0.01) \times 10^{17} \text{m}^{-2}$. The corresponding donor-acceptor centre-to-centre separation, d , is shown on the bottom axis. The blue solid line is the numerical simulation of the LSP coupled FRET using the Green's tensor formalism (eq 5.5). The conventional FRET efficiency expected for this donor-acceptor pair is also shown (black dashed line calculated using eq 5.2), with the same acceptor monolayer concentration and $R_0 = 4.2$ nm. The nonradiative energy transfer efficiency for the donor-Au NP bilayer based on the NSET formalism, with $d_0 = 3.1$ nm, is also included for comparison (black dotted line calculated using eq 5.3). (b) The dependence of the LSP coupled energy transfer rate on the separation, d .

radius in the trilayer structures compared with the Au NP-absent donor-acceptor bilayer, which validates that energy transfer range can be greatly extended with the aid of Au NPs.

The energy transfer rate between monolayers of donor and acceptor QDs can be derived by the FRET formalism as

$$k_{\text{FRET}} = \frac{C_{\text{Acc}}\pi R_0^6}{2d^4\tau_D} \quad (5.4)$$

and $k_{\text{LSP-FRET}} = \tau_{\text{Don,Tri}}^{-1} - \tau_{\text{Don,Au}}^{-1}$ can be calculated from measured decay lifetimes. The measured $k_{\text{LSP-FRET}}$ is presented in Fig 5.5 (b) as a log-log plot. The solid line is the result of the donor-acceptor centre-to-centre distance dependence of $k_{\text{LSP-FRET}}$ analyzed with the least-squares method. The linear fit indicates the existence of a constant R_0 for the fixed Au NP-donor spacer thickness and fixed Au NP concentration. The slope of $d^{-(4.0 \pm 0.4)}$ as well as the observation of d^{-4} separation dependence for the LSP coupled FRET efficiency indicate a similar d^{-4} distance dependence as conventional FRET-like separation dependence for bilayer structures [127, 162], given in eq. 6.5.

The PL spectra of all samples with varying acceptor-Au NP separation is shown in Fig 5.6 (a). Compared with Au-absent donor-acceptor bilayer, the donor emission is quenched less when the acceptor-Au NP spacer thickness increases. This agrees with the LSP coupled FRET efficiency dependence on acceptor-Au NP spacer thickness discussed earlier. Furthermore, acceptor emission is sensitive to the acceptor-Au NP spacer thickness. The corresponding PL ratio, $\frac{I_{\text{Acc,Tri}}}{I_{\text{Acc,BL}}}$ is presented in Fig 5.6 (b) as a function of the donor-acceptor centre-to-centre distance, d . Corresponding acceptor-Au NP spacer thickness is shown on the top axis. Furthermore, PL ratio, $\frac{I_{\text{Acc,Tri}}}{I_{\text{Acc,BL}}}$ for the varying donor-Au NP separation (spectra shown in Fig 5.3) is also presented as a function of d , on the bottom axis of Fig 5.6 with donor-Au NP spacer on top axis. The PL ratio expected for acceptor-Au NP bilayers with varying QD-Au NP separation relative to the emission for an acceptor monolayer, $\frac{I_{\text{Acc,Au}}}{I_{\text{Acc}}}$, is also shown for comparison. This acceptor PL ratio is calculated based on the NSET formalism using $d_0 = 5.7$ nm in eq 5.3. The value for d_0 was determined from experimental data for the acceptor-Au NP reference samples as presented in Chapter 4. In the trilayer samples quenching of the acceptor PL is observed for the shortest acceptor-Au NP separations. This suggests that direct quenching of the acceptor PL by the Au NPs is dominant despite the highest LSP coupled FRET efficiency and fastest LSP coupled FRET rates at the smaller acceptor-Au NP separations. At larger separations the acceptor PL in the trilayer structure increases, showing that the acceptor PL enhancement due to the LSP coupled FRET competes favorably with direct quenching of the acceptor emission by the Au NPs in this range.

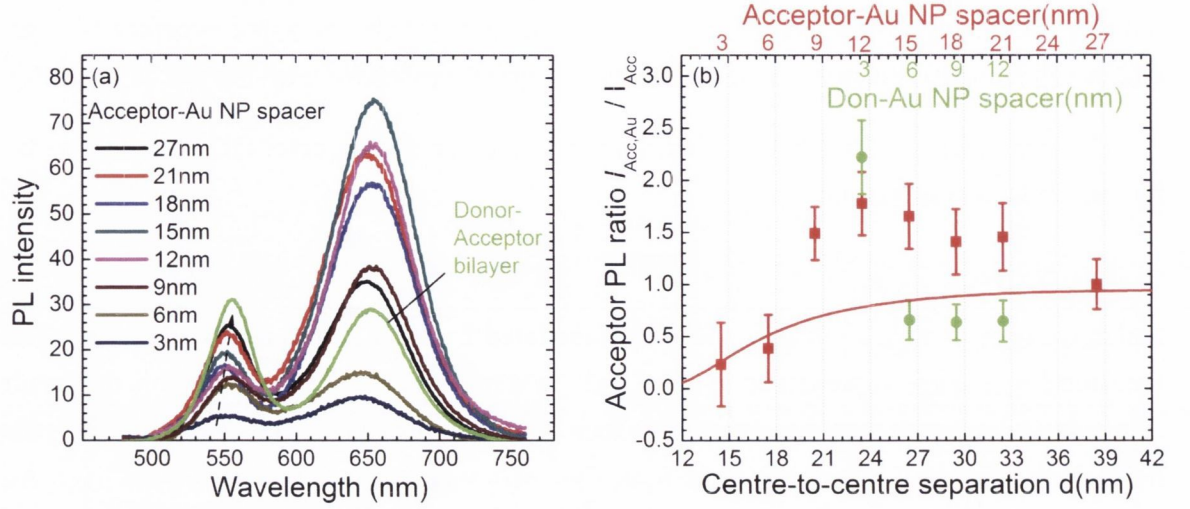


Fig. 5.6 (a) PL spectra of Acceptor-Au NP-Donor trilayer structures, which have a fixed donor-Au NP separation, $t_{Don-Au} = 3$ nm, and varying t_{Acc-Au} with $C_{Au} = (0.12 \pm 0.01) \times 10^{17} \text{m}^{-2}$. The QDs bilayer is also shown. (b) Acceptor PL ratio, $\frac{I_{Acc, Tri}}{I_{Acc, BL}}$ in trilayer structures, as a function of the donor-Au NP spacer thickness, t_{Acc-Au} (top axis, inner values), and donor-acceptor centre-to-centre distance, d , (bottom axis). The samples with a fixed acceptor-Au separation, $t_{Acc-Au} = 12$ nm, and varying t_{Don-Au} with $C_{Au} = (0.13 \pm 0.02) \times 10^{17} \text{m}^{-2}$ are shown as green circles. The samples with a fixed donor-Au NP separation, $t_{Don-Au} = 3$ nm, and varying t_{Acc-Au} with $C_{Au} = (0.12 \pm 0.01) \times 10^{17} \text{m}^{-2}$ are shown as red squares. The solid line is the calculated acceptor PL ratio, $\frac{I_{Acc, Au}}{I_{Acc}} = 1 - E_{NSET}$, for acceptor-Au NP bilayers, with the same separations and Au NP concentration as the varying acceptor-Au NP separation trilayer samples. This is calculated using eq. 5.3.

A maximum PL ratio of ~ 1.8 is observed for a $t_{Acc-Au} = 12$ nm. As the separation is further increased, the acceptor PL ratio reduces as the LSP coupled FRET contribution decreases.

The acceptor PL is more sensitive to the donor-Au NP separation, t_{Don-Au} , than the acceptor-Au NP separation, t_{Acc-Au} . For the same donor-acceptor centre-to-centre distance, d , maximum enhancement of the acceptor PL requires the smallest donor-Au NP separation. These observations are in agreement with the earlier results which showed that plasmon-donor coupling has a larger influence on LSP coupled FRET in this donor-Au NP-acceptor energy transfer system. The greater quenching of the acceptor PL in the trilayer structures with larger donor-Au NP separations, where the LSP coupled FRET efficiency is low and direct quenching by the Au NPs dominates, is due to the slightly higher Au NP concentration for that set of samples.

5.4 Au NP Concentration Dependence

As the LSP coupled FRET depends on Au NP concentration [30], to fully characterise the Au NP concentration dependence, two groups of samples are prepared, which includes a fixed donor-Au NP spacer thickness of $t_{Don-Au} = 3$ nm but (i) acceptor-Au NP spacer thickness $t_{Acc-Au} = 6$ nm; (ii) acceptor-Au NP spacer thickness $t_{Acc-Au} = 12$ nm, respectively.

The LSP coupled FRET efficiency, calculated by $E_{LSP-FRET} = 1 - \frac{\tau_{Don,Tri}}{\tau_{Don,Au}}$ is plotted in Fig 5.7 (a) as a function of Au NP concentration. It shows a strong dependence on Au NP concentration for both t_{Acc-Au} cases. The LSP coupled FRET efficiency with Acceptor-Au NP spacer layer separation $t_{Acc-Au} = 6$ nm is always larger than for $t_{Acc-Au} = 12$ nm at the similar Au NP concentration. It agrees with the observations shown in Fig 5.5.

As discussed earlier, LSP coupled FRET efficiency is dependent on Acc-Au NP layer separation which follows eq 5.2, $E_{FRET} = [1 + \frac{2d^4}{C_{Acc} \cdot \pi \cdot R_0^6}]^{-1}$. To compare two cases with $t_{Acc-Au} = 3$ nm and $t_{Acc-Au} = 6$ nm, the extracted R_0 by eq 5.2 is plotted in Fig 5.7 (b). The effective Förster radius increases with increasing Au NP concentration, and values as high as 10 nm are determined at the largest Au NP concentrations investigated. The conventional Förster radius, $R_0 = (4.2 \pm 0.4)$ nm for the donor-acceptor bilayer reference is shown at zero Au NP concentration. It is also observed that for fixed donor-Au NP separation, t_{Don-Au} , the dependence of the Förster radius on the Au NP concentration appears to be independent of the acceptor-Au NP separation, t_{Acc-Au} . This suggests that the donor-plasmon coupling is the dominant influence on the LSP coupled FRET efficiency. Furthermore, the trilayer structures with varying acceptor-Au NP separation, presented in Fig 5.5, had a Au NP concentration of $C_{Au} = (0.12 \pm 0.01) \times 10^{17} \text{ m}^{-2}$. This concentration corresponds to a Förster radius of (9 ± 1) nm from Fig 5.8 (b). This value agrees, within the error range, with the Förster radius obtain from fitting directly the donor-acceptor separation dependence of the LSP coupled FRET efficiency in Fig 5.5 using eq 5.2.

The PL ratio, $\frac{I_{Acc,Tri}}{I_{Acc,BL}}$ is plotted in Fig 5.8 as a function of the Au NP concentration for both acceptor-Au NP separations. Also plotted as solid lines are $\frac{I_{Acc,Au}}{I_{Acc,BL}}$ based on eq 5.3, $E_{NSET} = (1 + \text{const} \times d^2/C_{Au})^{-1}$ with $d_0 = 5.7$ nm. Despite direct quenching effect by Au NPs, the enhanced acceptor PL ratio, corresponding to a ratio >1 is observed at certain Au NP concentrations for both cases. Furthermore, the Au NP concentration with the maximum PL ratio is higher for $t_{Acc-Au} = 12$ nm than for $t_{Acc-Au} = 6$ nm. Additionally, the trilayer structure with $t_{Acc-Au} = 6$ nm shows greater sensitivity to the Au NP concentration in the form of a narrower peak in PL enhancement. The shift in the PL ratio peak to lower Au

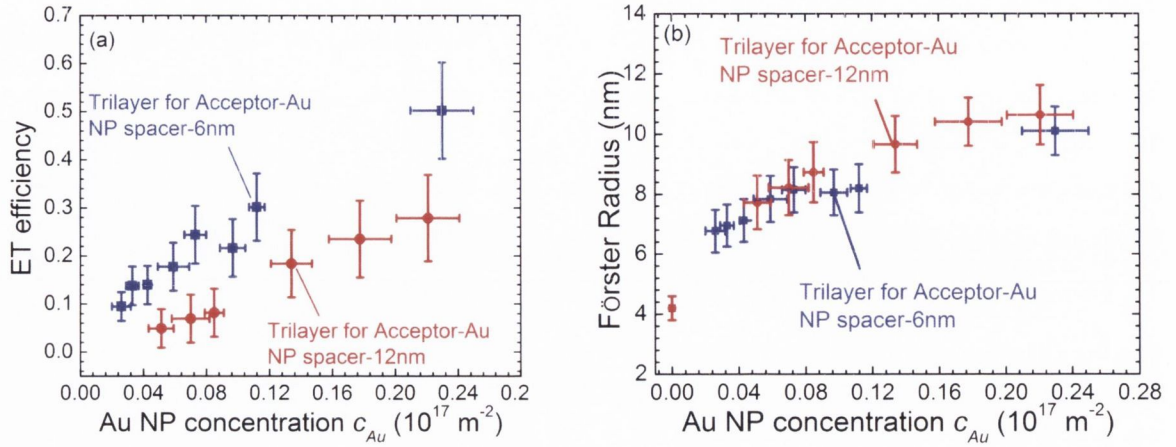


Fig. 5.7 (a) LSP coupled FRET efficiency as a function of the Au NP concentration. The acceptor-Au separations are $t_{Acc-Au} = 6 \text{ nm}$ (solid blue squares) and $t_{Acc-Au} = 12 \text{ nm}$ (solid red circles) with a fixed donor-Au NP separation $t_{Don-Au} = 3 \text{ nm}$. (b) Dependence of the extracted effective Förster radius for trilayer samples on the Au NP concentration. The acceptor-Au separations are $t_{Acc-Au} = 6 \text{ nm}$ (solid blue squares) and $t_{Acc-Au} = 12 \text{ nm}$ (solid red circles) with a fixed donor-Au NP separation $t_{Don-Au} = 3 \text{ nm}$.

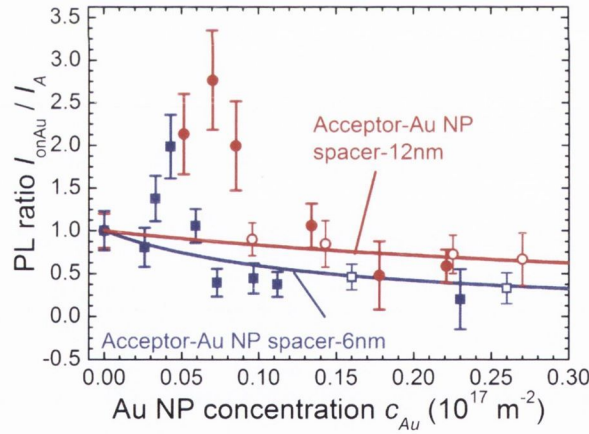


Fig. 5.8 PL ratio of the acceptor PL in a trilayer structure, $\frac{I_{Acc,Tri}}{I_{Acc,BL}}$ and the acceptor on Au NP structure, $\frac{I_{Acc,Au}}{I_{Acc}}$, as a function of the Au NP concentration. The trilayer samples with an acceptor-Au NP separation of $t_{Acc-Au} = 6 \text{ nm}$ (solid blue squares) and $t_{Acc-Au} = 12 \text{ nm}$ (solid red circles) have a fixed donor-Au NP separation, $t_{Don-Au} = 3 \text{ nm}$. Data for the acceptor-Au NP bilayer samples with an acceptor-Au NP separation of $t_{Acc-Au} = 6 \text{ nm}$ (open blue squares) and $t_{Acc-Au} = 12 \text{ nm}$ (open red circles) are also shown. The solid lines show the calculated acceptor PL ratio for acceptor-Au NP bilayers with the same separations using the NSET model (5.3).

NP concentrations and the increased sensitivity is a consequence of the interplay between the enhancement of the acceptor PL due to LSP coupled FRET and the direct acceptor PL quenching. The quenching due to nonradiative energy transfer from the QDs to the Au NPs is a function of both the acceptor-Au NP separation and the Au NP concentration. As seen earlier, in eq 5.3, the NSET efficiency has the form $E_{\text{NSET}} = (1 + \text{const} \times d^2/C_{\text{Au}})^{-1}$ and therefore, the increase in the quenching efficiency due to the reduction of the acceptor-Au NP separation from 12 nm to 6 nm, can be compensated by reducing the Au NP concentration. Consequently, the maximum acceptor PL enhancement will occur at a lower Au NP concentration, as observed.

5.5 Numerical Simulation

5.5.1 Green's tensor formalism

The Green's tensor of a Au nanosphere can be calculated from Mie theory. This can be extended to an ensemble of spheres through a multiple scattering method [195–197]. The Green's tensor couples to dipolar sources, which can approximate fluorophores such as fluorescent dyes and QDs. Once the Green's tensor of the ensemble (in our case a monolayer of Au NPs) is known, the LSP coupled energy transfer rate, $k_{\text{LSP-FRET}}$, is calculated directly from it *via* the following expression:

$$k_{\text{LSP-FRET}} = \tau_{\text{Don,Au}}^{-1} 36\pi^2 \Phi_{\text{Don}} \int_0^\infty d\lambda \lambda^{-2} f_{\text{don}}(\lambda) \sigma_{\text{Acc}}(\lambda) |\hat{n}_{\text{Don}} \cdot G(\hat{r}_{\text{Don}}, \hat{r}_{\text{Acc}}, \lambda \cdot \hat{n}_{\text{Acc}})|^2 \quad (5.5)$$

where G is the Green's tensor of the system, Φ_{Don} is the intrinsic quantum yield of the donor, f_{Don} and σ_{Acc} are the donor emission spectrum and acceptor absorption cross-section, respectively, and $\tau_{\text{Don,Au}}$ is the calculated donor lifetime in the presence of the Au NP ensemble [198]. The LSP coupled FRET efficiency, $E_{\text{LSP-FRET}}$, can then be obtained from

$$E_{\text{LSP-FRET}} = 1 - \frac{k_{\text{LSP-FRET}}}{\tau_{\text{Don,Au}}^{-1} + k_{\text{LSP-FRET}}} \quad (5.6)$$

All the inputs to the model are taken from experimental values, such as the Au NP and acceptor QD concentrations, the donor QD emission spectrum, acceptor QD absorption

spectrum, the donor quantum yield and spacer layer thicknesses. The measured quantum yield of the donor QD monolayer is 3%. A correction term has been added to the dielectric permittivity of Au NPs to account for finite-size effects. We have fitted this term to the experimental absorption spectrum of Au NPs in solution.

5.5.2 Donor-Au-Acceptor Trilayer Simulation

To model layered structures, as in the experimental samples, the energy transfer rate from a single donor to a layer of acceptors in the presence of the Au NP monolayer was calculated, where the energy transfer rates are averaged over a large number of realizations. The donor position in the donor monolayer has been randomly assigned.

The acceptor and Au NP monolayers have been constructed by randomly placing individual acceptors and Au NPs in their respective monolayers, with the specific concentrations used in experiments. The results of the numerical simulation for the LSP coupled FRET efficiency, $E_{\text{LSP-FRET}}$, as a function of $t_{\text{Don-Au}}$ is shown as the solid line in Fig 5.9 (a). The data presented here is the same data shown in Fig 5.4 (b). There is good agreement between the theoretical and experimental results. It should be noted that the numerical model is not a fit, there are no free parameters, as discussed above.

Using the Green's tensor approach described earlier, the calculated numerically LSP coupled energy transfer efficiencies for the fixed donor-Au NP separation and varying acceptor-Au NP separation are shown as the solid line in Fig 5.9 (b). As before the theoretical results are in good agreement with the trilayer LSP coupled FRET efficiency experimental data. The agreement of the numerical simulation with experimental data, shown in both Fig 5.9 (a) and Fig 5.9 (b), validates the model.

5.5.3 A Single Donor-Au NP-Acceptor Triad Simulation

The model is then applied to investigate the energy transfer efficiency for a single donor-Au NP-acceptor triad. The donor QD and acceptor QD are placed on opposite sides of the Au NP and have the same properties as in the trilayer samples. The numerical results for the donor-acceptor energy transfer efficiency, $E_{\text{LSP-FRET}}$, as a function of the donor-acceptor centre-to-centre distance, d , are shown in Fig 5.10. Two cases are considered, firstly, the donor-Au NP separation, $t_{\text{Don-Au}}$, is kept fixed and the acceptor-Au NP separation, $t_{\text{Acc-Au}}$, is varied, and secondly, $t_{\text{Acc-Au}}$ is kept fixed with varying $t_{\text{Don-Au}}$, shown in Fig 5.10 (a) and (b), respectively. In Fig 5.10 (a) the numerical simulation results are shown for two values of $t_{\text{Don-Au}}$, 3 nm and 6 nm. The case of a single donor-acceptor pair, in the absence

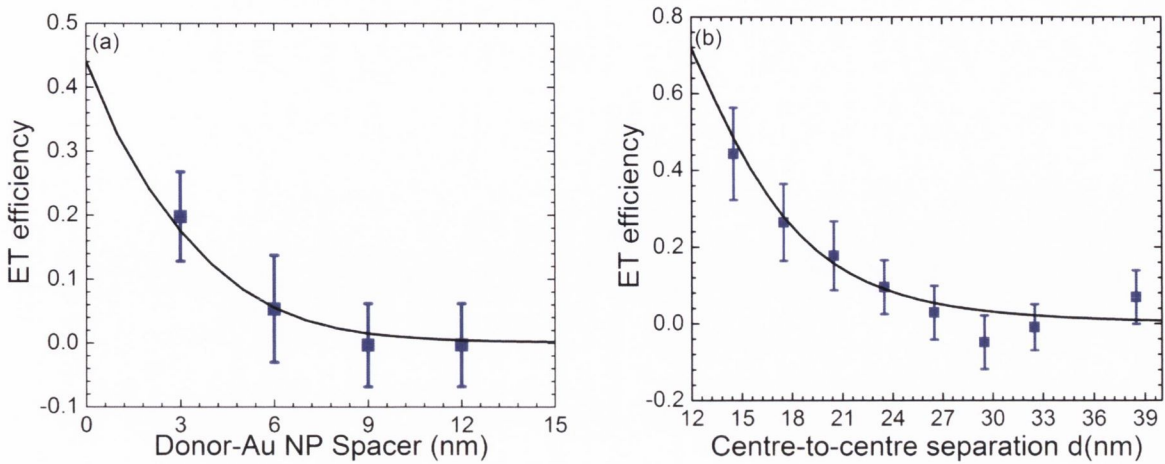


Fig. 5.9 (a) The LSP-coupled FRET efficiency $E_{\text{LSP-FRET}}$ as a function of donor-Au NP spacer layer thickness. The data was measured with a fixed Acceptor-Au spacer thickness, $t_{\text{Acc-Au}} = 12$ nm, as presented in Fig 5.4. (b) The LSP coupled energy transfer efficiency as a function of the centre-to-centre distance, d . The data was measured with a fixed donor-Au spacer thickness, $t_{\text{Don-Au}} = 3$ nm, as presented in Fig 5.5 (a). The solid lines are calculated from numerical simulation.

of a Au NP is also shown as a reference. The lines shown in Fig 5.10 (a) correspond to fitting the numerical simulation data with a conventional FRET model for the energy transfer efficiency for a single donor-acceptor pair,

$$E_{\text{FRET}} = \frac{1}{1 + \left(\frac{d}{R_0}\right)^6} \quad (5.7)$$

The fitting shows that over one order of magnitude of the donor-acceptor centre-to-centre separation, d , the Au NP-mediated donor-acceptor interaction closely resembles conventional FRET ($n = 6$), but with an increased Förster radius, R_0 . For the two donor-Au NP distances investigated, $t_{\text{Don-Au}} = 3$ nm and $= 6$ nm, the corresponding Förster radii are $R_0 = 8.2$ nm and $R_0 = 6.8$ nm, respectively. Comparing this with the Förster radius of the donor-acceptor pair in the absence of the Au NP, $R_0 = 4.3$ nm, we see that the Förster radius can be nearly doubled, depending on the donor-Au NP separation, $t_{\text{Don-Au}}$. As the donor is moved further from the Au NP, the enhancement of the Förster radius becomes less and less prominent, eventually vanishing. It can be noted that the Förster radius of 4.3 nm obtained for the donor-acceptor pair is in agreement with the experimentally determined Förster radius $R_0 = (4.2 \pm 0.4)$ nm, which was discussed earlier.

Fig 5.10 (b) shows the same calculated energy transfer efficiency dependence on the donor-acceptor separation, d , but now it is the acceptor-Au NP spacer thickness, $t_{\text{Acc-Au}}$,

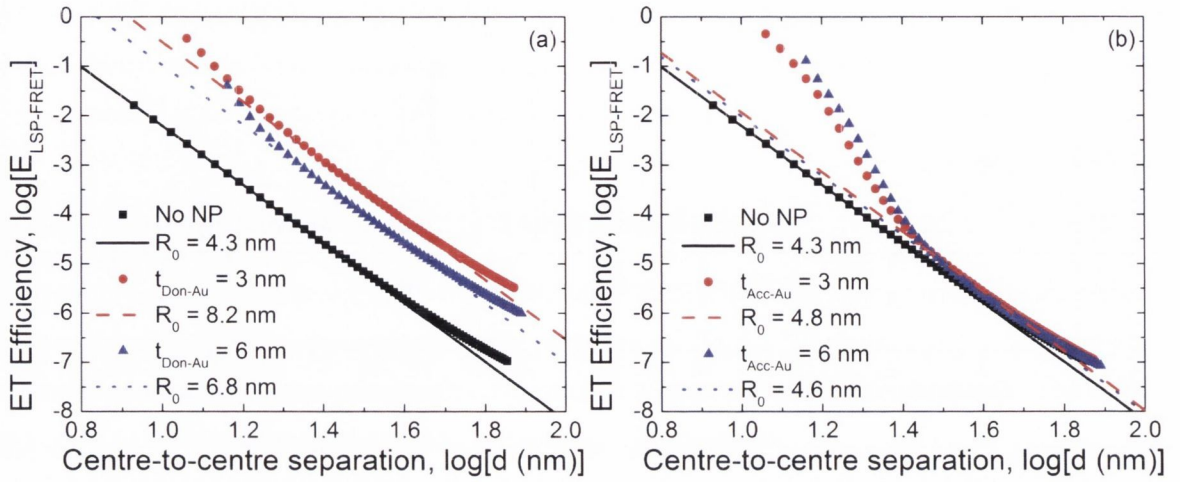


Fig. 5.10 (a) Calculated LSP coupled energy transfer efficiency, $E_{\text{LSP-FRET}}$, as a function of the donor-acceptor centre-to-centre separation, d , with fixed donor-Au NP separations $t_{\text{Don-Au}} = 3$ nm (red circles) and 6 nm (blue triangles). The symbols represent the numerical simulation results calculated using the Green's tensor formalism. The lines represent the fit of these results with a FRET model given by eq 5.7. (b) Calculated LSP coupled energy transfer efficiency, $E_{\text{LSP-FRET}}$, as a function of the donor-acceptor centre-to-centre separation, d , for fixed acceptor-Au NP separations $t_{\text{Don-Au}} = 3$ nm (red circles) and 6 nm (blue triangles). Both axes are logarithmic. The case of a single donor-acceptor pair, without a Au NP is also shown (black circles) as a reference in both panels.

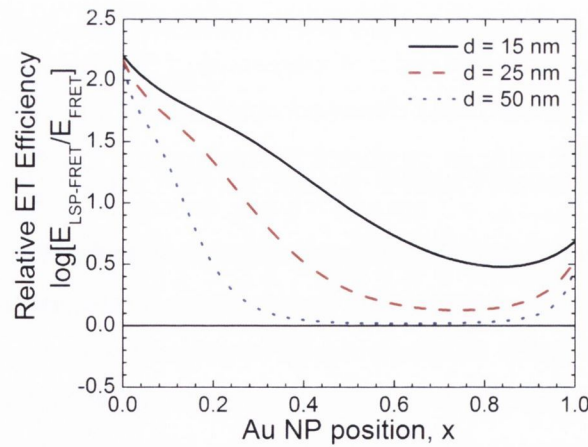


Fig. 5.11 Relative energy transfer efficiency as a function of the intermediate Au NP position between the donor and acceptor QDs, for several fixed donor-acceptor centre-to-centre distances, d .

which is kept fixed while the donor-Au NP spacer thickness, t_{Don-Au} , increases. Two values of t_{Acc-Au} are considered, 3 nm and 6 nm. In this case it is seen that the FRET model is only valid over a much smaller range of d . Furthermore, within this range the fitting shows only a very small enhancement of the Förster radius from $R_0 = 4.3$ nm to $R_0 = 4.8$ nm for $t_{Acc-Au} = 3$ nm and $R_0 = 4.6$ nm for $t_{Acc-Au} = 6$ nm. The increase in the LSP coupled FRET efficiency at the lower values of d corresponds to where the donor and Au NP are sufficiently close that the LSP coupled FRET is once again strongly influenced by the donor-plasmon coupling. Comparison of Fig 5.10 (a) and (b) shows that the donor-acceptor interaction in the presence of the Au NP is more sensitive to t_{Don-Au} than it is to t_{Acc-Au} . This is manifest in the greater sensitivity of the energy transfer efficiency, $E_{LSP-FRET}$, to the change in t_{Don-Au} for a fixed t_{Acc-Au} compared with modification of $E_{LSP-FRET}$ for changing with a constant t_{Don-Au} .

To further investigate the influence of the placement of the Au NPs on the LSP coupled energy transfer mechanism, the LSP coupled FRET efficiency between the donor and acceptor is calculated as a function of the position of an intermediate Au NP for a three values of donor-acceptor separation, d . The results are shown in Fig 5.11. To facilitate direct comparison of the effect of the position of the Au NP for different values of d , we plot the relative energy transfer efficiency, which is ratio of the energy transfer efficiency between the donor QD and acceptor QD in the presence of the Au NP, $E_{LSP-FRET}$, and in the absence of the Au NP, E_{FRET} . To plot the data for a number of different values of d on the same graph, the intermediate Au NP position is presented as a fraction, x . This fraction is given by $x = \frac{t_{Don-Au}}{[d - (r_{don} + r_{Acc} + 2 \times r_{Au})]}$ and can vary from 0 to 1, where $x = 0$ and $x = 1$ correspond to the Au NP adjacent to the donor and acceptor, respectively.

It is clearly evident from Fig 5.11 that the LSP coupled FRET efficiency is more enhanced when the Au NP is close to the donor ($x \sim 0$) rather than when it is close to the acceptor ($x \sim 1$). Furthermore, the LSP coupled FRET efficiency with the Au NP close to the donor extends further than for Au NP closer to the acceptor. For smaller values of d there is evidence of QD-plasmon coupling for all positions of the Au NP, as demonstrated by the fact that the logarithm of the relative energy transfer efficiency does not go to zero, i.e. the LSP coupled energy transfer efficiency is enhanced compared with its value in the absence of the Au NP. For $d = 50$ nm, the Au NP can be placed sufficiently far from both the donor and acceptor QDs such that neither QD is coupled to the Au NP, and the energy transfer efficiency is the same as in the absence of the Au NP.

5.6 Conclusion

It has been demonstrated that the signatures of LSP coupled FRET between donor and acceptor QD planes depend strongly on the position of an intermediate Au NP monolayer and the Au NP concentration.

The dependence of the LSP coupled FRET efficiency on the separations between the three components of the system has been experimentally investigated. The largest LSP coupled FRET rates and efficiencies are observed for the higher Au NP concentration, smallest donor-Au NP and acceptor-Au NP separations. However, LSP coupled FRET through the intermediate Au NP layer is observed to be more sensitive to the donor-Au NP separation. It was experimentally observed that the dependence of the LSP coupled FRET efficiency on the donor-acceptor separation has the same d^{-4} form as conventional FRET. The independence of the Förster radius on the acceptor-Au NP separation indicates a LSP coupled FRET system in which donor-plasmon coupling is dominant. The dipole-dipole behavior of the separation dependence of the LSP coupled FRET efficiency suggests that the strongly coupled donor-plasmon system can be considered as an enhanced donor dipole. The possibility to engineer systems with a well-defined distance dependence has potential as a long-range spectroscopic ruler or for sensing applications. The characteristic energy transfer distance can be tuned through the Au NP concentration. For any acceptor-Au NP separation the Au NP concentration can be adjusted to optimize the LSP coupled FRET enhanced acceptor PL. The large enhancement of the acceptor emission reported, despite competition with direct quenching by the Au NPs, demonstrates that LSP coupled FRET could be suitable for light emitting device application. Complimentary theoretical studies confirmed and further elucidated the experimental observations.

Chapter 6

Localised Surface Plasmon Mediated Energy Transfer in Hybrid Quantum Well-Quantum Dot System

As mentioned in Chapter 2, Quantum well (QW) pumping quantum dots (QDs) through Förster resonance energy transfer (FRET) [15] plays an important role in various optoelectronic devices but suffers a limited FRET range ~ 10 nm. The FRET efficiency is quite weak at larger distance between QW and QDs. Therefore, only one proximal QW can contribute to QDs through nonradiative energy transfer. QDs can be only placed in close proximity to QW and the capping layer of QW should be as thin as possible. However, a thin capping layer limits the carrier injection efficiency of the QW. Dry-etched nanopillar [17, 74, 75] QW structure and QW hybrid with graded QDs [74] are reported to obtain higher energy transfer efficiency through architecture optimization. Based on the localised surface plasmon (LSP) enhanced energy transfer in QDs system as discussed in Chapter 5, here we propose a new approach to overcome the trade-off in the capping layer thickness, to improve FRET efficiency and break the distance limit of the FRET in QW-QD system.

In order to study LSP coupled energy transfer, colloidal Au nanoparticle (NP) monolayer is built between QW and CdTe QD monolayer, which has been proposed as the optimum geometry for LSP coupled FRET [54]. The schematic can be seen in Fig 6.1. The single InGa_N quantum wells are prepared by metal-organic chemical-vapor deposition on sapphire substrate, which consists of a GaN buffer layer, InGa_N QW (~ 2 nm) and a final GaN capping layer (~ 3 nm). Hybrid QW-Au-QD samples are prepared by layer-by-layer assembly. Details of the polyelectrolytes (PE) can be found in Chapter 3. Single InGa_N QW with emission wavelength centered at ~ 520 nm is the energy transfer donor while QDs

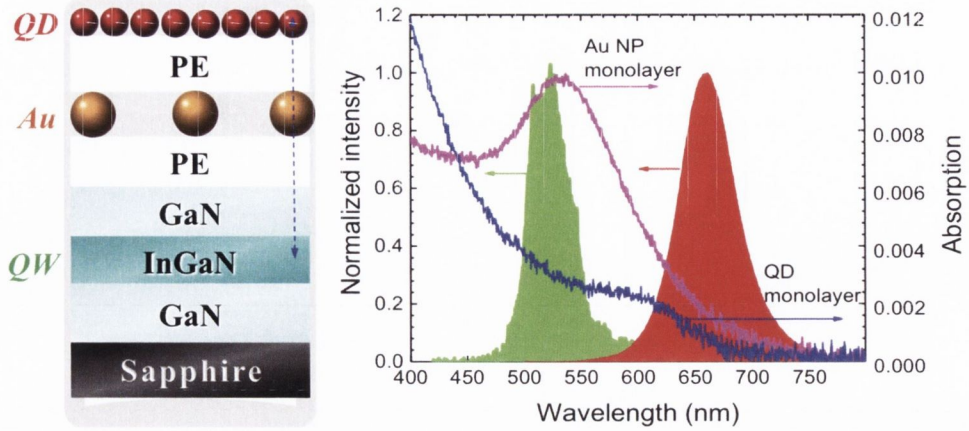


Fig. 6.1 Schematic of QW-Au-QD hybrid geometry is shown in the left. Polyelectrolytes (PE) are deposited between QW and Au NP monolayer, and between Au NP and QD monolayers. The normalized emission spectra (left-axis) of single InGaN quantum well (green) and QD monolayer (red) are shown. The absorption spectra (right-axis) of QD monolayer (blue line) and Au NP monolayer (purple line) are also shown.

with emission wavelength centered at ~ 660 nm are the acceptors. The absorption peak of the Au NP monolayer is at ~ 532 nm. It can be seen in Fig 6.1 that there is good spectral overlap of the donor QW emission and acceptor QD absorption to enable efficient FRET. Furthermore, QW and QD emission spectra overlap well with LSP absorption of the Au NP monolayer in order for the coupling of LSP and FRET. As the incorporation of the Au NPs will modify the emission properties of donor and acceptor, which has been studied in Chapter 4, the interaction of donor QW and Au NP monolayer needs to be clarified first for the clear signatures of LSP coupled FRET. Therefore, the characterisation of QW-only, QW-Au NPs will be presented first, finally QW-Au-QD system will be studied.

6.1 QW-only Characterisation

To characterise the QW samples, the excitation power-dependent PL decay measurements are undertaken. The emission intensity is measured from the PL decay curves at $t = 0$ ns. All the lifetimes mentioned here are the average lifetime determined from bi-exponential fits of the time-resolved PL traces [127].

The injected carrier density in QW, n is proportional to the excitation power, which is calculated based on the eq 6.1

$$n = \frac{P}{(\hbar\omega) \cdot S \cdot d_{\text{InGaN}} \cdot \gamma} \cdot e^{-\alpha_{\text{GaN}} d_{\text{GaN}}} \cdot [1 - e^{-\alpha_{\text{InGaN}} d_{\text{InGaN}}}] \cdot (1 - R) \quad (6.1)$$

where $\hbar\omega$ is the excitation photon energy, S is the spot size of the pumping laser with $S = 0.43\mu\text{m}$, R is the reflection coefficient. α is the absorption efficiency, d is the thickness. Experimentally, we use $\lambda = 400\text{ nm}$ (3.1 eV) to excite the InGaN QW only without pumping GaN (3.4 eV) barrier with $\alpha_{\text{GaN}} = 0$. $\alpha_{\text{InGaN}} = 10^5\text{cm}^{-1}$ is quoted from [199], $d_{\text{InGaN}} = 2\text{ nm}$ and $\gamma = 10\text{ MHz}$.

The PL intensity and decay lifetime vs injected carrier density are shown in Fig 6.2 (a) (b) respectively. The carrier dynamics depends strongly on the carrier density, which are determined by the population of free carriers, heavy and light free excitons, and bound excitons [200, 201]. The PL intensity depends linearly on the carrier density at lower carrier density regimes while a quadratic dependence is present at higher carrier density. The quadratic dependence is characteristic of free-carrier bimolecular recombination. Furthermore, at the lower carrier density regime, there is an increase of decay lifetime, which is attributed to the capture of carriers by defect states where nonradiative recombination dominates [199]. At higher carrier density regime, the decay lifetime decreases with increasing carrier density where the defect states seems saturated as shown in Fig 6.2 (b). The radiative recombination becomes prevailing in this regime.

In order to unravel the physics underlying the lifetime reduction in the radiative recombination dominant regime, a rate model is adopted. The instantaneous PL decay rate or the inverse of decay lifetime τ_{PL}^{-1} as a function of n_0 , which is the generated carrier at $t = 0$ ns is given by [200]

$$\frac{1}{\tau_{PL}} = \left| \frac{d \log(I_{PL})}{dt} \right|_{t=0} = 2(A + Bn_0) \quad (6.2)$$

where $I_{PL} = Bn^2$ is taken based on the rate model as

$$\frac{dn}{dt} = -An - Bn^2 - Cn^3 \quad (6.3)$$

where $A(\text{s}^{-1})$, $B(\text{cm}^3\text{s}^{-1})$, $C(\text{cm}^6\text{s}^{-1})$ are the Shockley-Read-Hall nonradiative recombination, the radiative recombination and the Auger recombination coefficient, respectively. Here the cubic Auger recombination is neglected as this becomes significant only at much higher excitation powers [202]. Therefore, in the lower carrier density regime, gradually reduction of decay lifetime results from the increasing carriers, which decay radiatively. It also validates that the radiative decay dominates in this regime. Since FRET is in essence nonradiative energy transfer, we focus on the lower carrier density regime ($< 10^{18}\text{cm}^{-3}$) to study LSP coupled FRET, which competes with the QW's nonradiative losses.

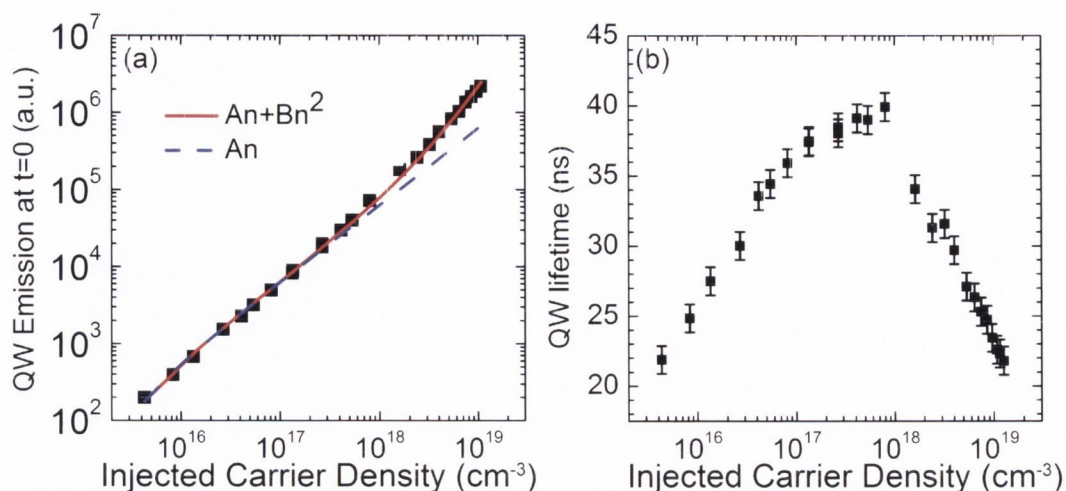


Fig. 6.2 The PL intensity at $t = 0$ ns time delay (a) and decay lifetime (b) as a function of injected carrier density. (The PL decay curves of QW-only are measured by Luke Higgins.)

6.2 QW Modification by Au Nanoparticles

In order to analyse QW-Au NP-QD structure finally, the modification of the optical properties of the QW needs to be clarified. Thus the hybrid QW-Au NP structures are built. Colloidal Au NPs have an average diameter of 5.5 nm stabilized by 4-dimethylaminopyridine (DMAP) [172]. The small QW pieces ($\sim 4 \text{ mm} \times 4 \text{ mm}$) are cut from one wafers. They are immersed in isopropyl alcohol (IPA) with ultrasonic bath for 1 min to remove any contaminations as well as surfaces oxides. Then they are kept in the millipore water to minimize exposure to the air before layer-by-layer deposition. A polyelectrolytes (PDDA+PSS) (~ 2.5 nm) layer is positioned between QW and Au NP monolayer. Identical preparation is carried out simultaneously on quartz to measure absorption. The PE thickness can be obtained from the absorption of PE layer. The calibrated curve of measured PE thickness vs PE absorption value can be found in Sect. 3.1.2, Chapter 3.

A QW sample with PE layer is built as the reference sample to take into account the influence of surface related states on the carrier dynamics [203]. As can be seen from Fig 6.3 (a), the QW-only has an average decay lifetime of $\tau_{QW} = 40$ ns while QW-Au becomes $\tau_{QW,Au} = 27$ ns at the carrier density of $1.8 \times 10^{16} \text{ cm}^{-3}$. The reduction of the decay lifetime indicates that Au NPs introduces another decay channel, which accelerates the QW decay. The energy transfers from the QW to Au NPs and the energy transfer competes with other recombination decay rates. Due to large separation of QW and Au NP monolayer, charge transfer or radiative energy transfer is ruled out for the shortening of decay lifetime. Therefore, the nonradiative energy transfer efficiency and rate can be measured from decay lifetime

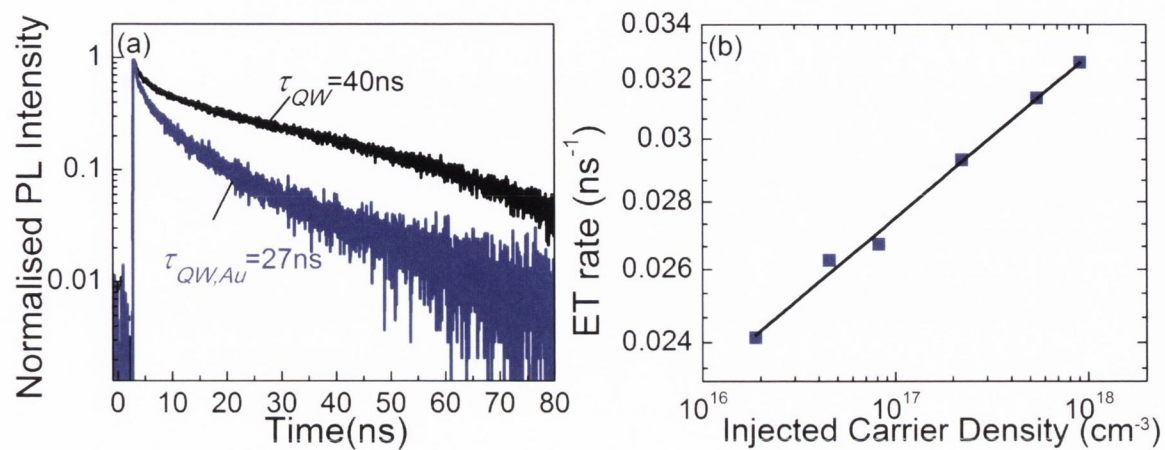


Fig. 6.3 (a) Normalized PL decay profiles of InGaN QW in the absence (black) and presence of Au NPs. (b) Energy transfer decay rate extracted from the decay lifetime, $k_{ET} = \tau_{QW,Au}^{-1} - \tau_{QW}^{-1}$, as a function of injected carrier density.

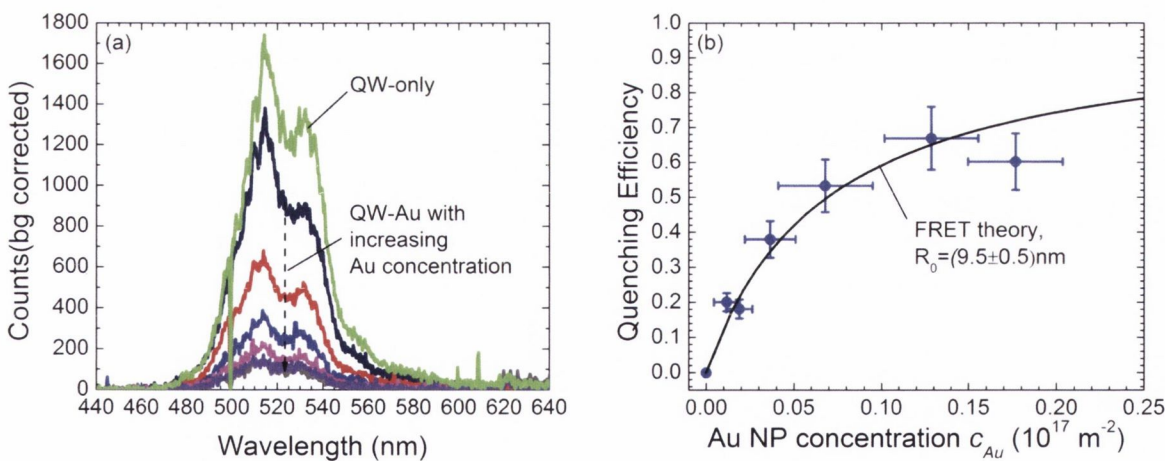


Fig. 6.4 (a) Emission spectra of QW-only and QW-Au with varying Au NP concentration. (b) Au NP concentration dependence of the quenching efficiency, E_{ET} , of QW, on top of which is assembled by a Au NP monolayer. The energy transfer efficiency was determined from the average decay lifetime quenching. The solid line (black) represents the fit of the quenching efficiency with a model based on the FRET mechanism.

changes. In the absence of Au NPs, the decay rate of QW is $k_{QW} = k_r + k_{nr} = \tau_{QW}^{-1}$ while for QW-Au NP structure, the decay becomes $k_{QW,Au} = k_r + k_{nr} + k_{ET} = \tau_{QW,Au}^{-1}$. Therefore, the energy transfer rate and efficiency is calculated from

$$E_{ET} = \frac{k_{ET}}{k_r + k_{nr} + k_{ET}} = 1 - \frac{\tau_{QW,Au}}{\tau_{QW}} \quad (6.4)$$

$$k_{ET} = k_{QW} - k_{QW,Au} = \tau_{QW}^{-1} - \tau_{QW,Au}^{-1} \quad (6.5)$$

The energy transfer efficiency in Fig 6.3 (a) is $E_{ET} = 32\%$ while $k_{ET} = 0.012 \text{ ns}^{-1}$. The energy transfer rate calculated by Eq 6.5 is plotted in Fig 6.3 (b) as a function of excitation power, the linear dependence indicates that the carriers generated in QW is not excitonic but free [15]. It has similar observations in the hybrid QW-QD or QW-organic material system reported in Ref. [15, 165]. Au NP monolayers with varying concentration are deposited on top of the QW. Identical metal NP monolayers are prepared on quartz substrate for measuring Au NP concentration. The energy transfer efficiency calculated by eq 6.4 is shown in Fig 6.4 (b) for varying Au NP concentration.

Since we have discussed in Chapter 4 that Au NP concentration has effect on the energy transfer efficiency. The Au NP concentration dependent energy transfer efficiency or rate can be described within FRET and NSET model if the donor emission wavelength on resonance with the LSP absorption of the Au NPs. Here we use FRET just to characterise the lifetime modification of QW by Au NPs in the QW-Au NP structure, which will be later compared with the QW-Au NP-QD structure. For randomly distributed Au NP monolayer, the energy transfer efficiency can be expressed as

$$E_{FRET} = \frac{1}{1 + \frac{2d^4}{C_{Au} \cdot \pi \cdot R_0^6}} \quad (6.6)$$

where d is the minimum separation of the QW and Au NP monolayer with $d = t + d_{QW}/2 + r_{Au} + r_{cap} = 9.25 \text{ nm}$, which includes the PE thickness, $t = 2.5 \text{ nm}$, half width of QW $d_{QW}/2 = 1 \text{ nm}$, capping layer of QW, $r_{cap} = 3 \text{ nm}$, as well as radius of Au NP, $r_{Au} = 2.75 \text{ nm}$. C_{Au} is the Au NP concentration. R_0 is the fitting parameter. The data shown in Fig 6.3 (b) is fitted by FRET model with fitting parameter $R_0 = (9.5 \pm 0.5) \text{ nm}$. For any FRET pair, R_0 can be calculated by its inherent spectral properties as

$$R_0 = 0.211 \left[\frac{\kappa^2 \Phi_{QW} J(\lambda)}{n^4} \right]^{\frac{1}{6}} \quad (6.7)$$

where κ^2 is an orientation factor between the donor and acceptor, $\kappa^2 = 2/3$ for isotropic system. Φ_{QW} is the quantum yield of the QW, n is the refractive index of the surrounding medium $J = \int_0^\infty \hat{f}_D(\lambda) \cdot \epsilon_{Au}(\lambda) \cdot \lambda^4 d\lambda$, in which $\hat{f}_D(\lambda)$ is the area-normalized donor QW emission spectrum as shown in Fig 6.1 (b).

The quantum yield of QW can be experimentally obtained through decay lifetime measurement [204]. As shown in Fig 6.3 (a), QW has an average decay lifetime of 40 ns by bi-exponential fitting. The decay has a short decay component as $\tau_{\text{short}} = 2.63$ ns while a long component as $\tau_{\text{long}} = 48.7$ ns. Generally, the short decay lifetime is related to intrinsic radiative decay while long component is related to nonradiative decay [204], the quantum yield is calculated as $\Phi_{QW} = \frac{k_r}{k_r + k_{nr}}$ with $k_r = \tau_{\text{short}}^{-1}$ while $k_{nr} = \tau_{\text{long}}^{-1}$. $\Phi_{QW} = 95\%$ is obtained for the QY. From spectral overlap based on eq 6.7, $R_0 = (10 \pm 0.2)$ nm is calculated, which agrees with that from experimental fitting in error range shown in Fig 6.4 (b). At such large separation of QW-Au NP with $d = 9.25$ nm, a maximum of 60% is achieved, which greatly extends the traditional energy transfer ranges, such as in QD-QD pair, FRET has a limitation of ~ 10 nm.

6.3 QW-Au-QD Hybrid Structure

The CdTe QDs, stabilized by thioglycolic acid, were synthesized in water according to standard procedures [171, 205]. The QD used in this Chapter is QD-5, the details of QD-5 solution can be found in Appendix A. Since we have investigated the direct interaction between QW and Au NP monolayer as shown above, next we investigate the interaction in a QW-Au-QD geometry, where a monolayer of QDs ($\lambda_{em} = 660$ nm) is assembled on top of QW-Au samples with spacer thickness of 6 nm.

The decay profiles of QW-Au NP bilayer before and after the QD deposition are both measured. As shown in Fig 6.5 (a), the emission intensity ($t = 0$ ns) is reduced. Furthermore, the decay lifetime decreases from 17.5 ns to 13.8 ns in Fig 6.5 (a), which indicates that QDs add another relaxation channel for the QW in the presence of QDs. In the hybrid QW-Au-QD system, the distance of QW and QD is $d = d_{QW}/2 + r_{cap} + d_{Au} + t_{PE} + r_{QD} = 20.2$ nm, which includes half width of the InGaN QW, $d_{QW}/2 = 1$ nm, capping GaN thickness, $r_{cap} = 3$ nm, the diameter of Au NP, $d_{Au} = 5.5$ nm, PE layer thickness used separating QW and Au NP monolayer, 2.5 nm as well as that separating Au NP monolayer and QD monolayer, 6 nm with $t_{PE} = 8.5$ nm, and the radius of QD r_{QD} . $R_0 = (5.2 \pm 0.3)$ nm is calculated for the QW-QD pair from spectral overlap of QW emission spectrum and acceptor QD extinction spectrum. At such large distance (~ 20.2 nm) between QW and QD monolayer, the

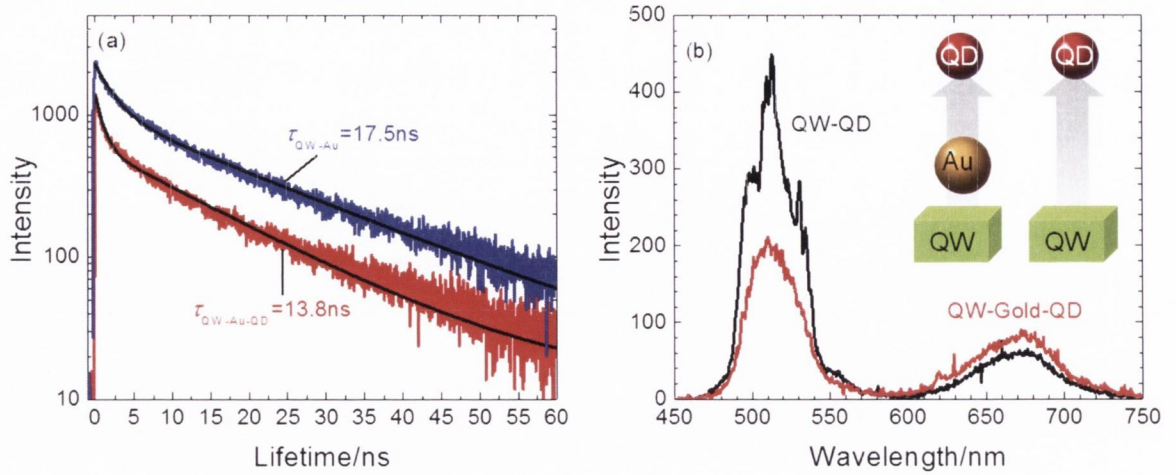


Fig. 6.5 (a) The PL decay profiles of QD-Au structures with (red) and without (blue) QDs. (b) Emission spectra of QW-Au-QD and QW-QD structure. Schematic is also shown.

traditional FRET is negligible. Therefore, with the aid of Au NPs, LSP enhances energy transfers from QW to QDs. The LSP mediated energy transfer efficiency can be calculated as $E_{\text{LSP-FRET}} = 1 - \frac{\tau_{\text{QW-Au}}}{\tau_{\text{QW-Au-QD}}} = 19\%$. As it has been demonstrated that the nonradiative energy transfer from QW to QDs can be described by FRET [15], the energy transfer efficiency can be described as

$$E_{\text{FRET}} = \frac{1}{1 + \frac{2d^4}{C_{\text{QD}}\pi R_0^6}}, \quad (6.8)$$

where C_{QD} is the acceptor QD concentration. Both E_{FRET} and d are experimentally measured. $R_0 = 8.9$ nm, which is the LSP coupled FRET distance, is obtained from eq 6.8. Thus a ~ 1.9 fold enhancement of the Förster radius is obtained compared with Au-absent QW-QD FRET pair. As LSP mediated FRET distance is dependent on Au NP concentration as well as donor-Au distance, which have been studied in Chapter 5. The FRET range can be further extended by tuning the Au NP concentration or the Au NP position.

Furthermore, the emission of QW-QD structure as well as QW-Au-QD samples are presented in Fig 6.5 (b). QD monolayer is separated from QW using six bilayer of (PDDA/PSS) in QW-QD sample ($d \sim 20.7$ nm) to obtain similar separation in QW-Au-QD (20.2 nm) sample. Despite the direct quenching by Au NPs, a ~ 1.47 fold QD emission enhancement is observed in QW-Au-QD sample compared with the Au-absent QW-QD sample. As there is no direct QD emission enhancement by Au NP, which has been discussed in Chapter 5, the emission enhancement results from LSP coupled FRET from QW to QD monolayer.

Considering the QW-based devices applications, the optimisation of the QW-Au NP-QD

geometry depends on whether the device requires higher FRET efficiency, larger distance or higher QD emission, which can be tuned by Au NP concentration or the Au position. It may have the potential for LSP enhanced FRET in QW device applications.

6.4 Conclusion

In conclusion, we have characterised single InGaN QW at room temperature through PL spectra as well as decay lifetime measurements. In the lower excitation power regime, nonradiative decay dominates while at higher excitation power radiative decay dominates.

The QW-Au structure is characterised. The emission and decay lifetime quenching have been observed, the quenching efficiency is considered within FRET model. The R_0 obtained from experimental observations is in good agreement with that calculated from FRET theory, which proves that the lifetime modification results from nonradiative energy transfer. The energy transfer rate from the QW to Au NPs with a fixed concentration goes up linearly with excitation power, which indicate that free carriers are generated in QW donor.

Finally, QW-Au-QD structure is built. LSP couple FRET in QW-Au NP-QD hybrid structure is observed. With the aid of LSP, a ~ 1.9 fold enhancement of R_0 is obtained, which greatly extends the QW-QD interaction range as a FRET pair. It makes it possible for the QW pumping QDs through nonradiative energy transfer over larger distances. Furthermore, a ~ 1.47 fold QD emission enhancement is obtained, which may enable the applications in QW-QD based color converters or light emitting diodes overcoming design issues related to the limited energy transfer distances.

Chapter 7

Summary and Future Work

Energy Transfer from Quantum Dot monolayer to Au Nanoparticle Monolayer

The energy transfer from QD monolayer to a Au NP monolayer has been observed as discussed in Chapter 4. The Au nanoparticle (NP) with the diameter of 5.5 nm has the localised surface plasmon (LSP) absorption peak at ~ 532 nm in monolayer. The emission as well as lifetime quenching are observed. The quenching efficiency calculated from lifetime quenching agrees that calculated from emission quenching, indicating the energy transfer is mainly nonradiative energy transfer. Five different sized CdTe QDs with the emission wavelengths varying from 534 nm to 660 nm are paired with Au NPs to probe the donor emission wavelength dependence. Stronger quenching is observed for the QDs red-shift 120 nm with respect to the LSP absorption peak of the Au NP monolayer than on resonance with LSP absorption peak.

Förster resonance energy transfer (FRET) and nanometal surface energy transfer (NSET) formalisms are derived for the planar geometry (we used in this thesis) from that for a single donor-acceptor pair. The distance as well as Au NP concentration dependent quenching efficiency can be fitted by both FRET and NSET formalisms. The characteristic distance, R_0 for FRET and d_0 for NSET are obtained from the fitting of the experimental data. Compared with R_0 and d_0 from theoretical expectations, a closer agreement is found for NSET theory for all the QD emission wavelength range. A good FRET agreement is only found for the QD emission wavelength on resonance with the LSP absorption peak but a poor agreement for that off-resonance with the LSP absorption peak. The experimental observations suggests that the NSET formalism can be a convenient phenomenological tool for the analysis of emission quenching due to nonradiative energy transfer to a plane of metal NPs.

Looking forward, why a Au NP with the diameter of 5.5 nm, which has comparable size with the QDs, can be regarded as a surface still need more studies. Furthermore, a stronger quenching for the QD with emission red shift with respect to the LSP absorption peak also need theoretical explanation.

Localised Surface Plasmon Mediated Energy Transfer in Quantum Dots

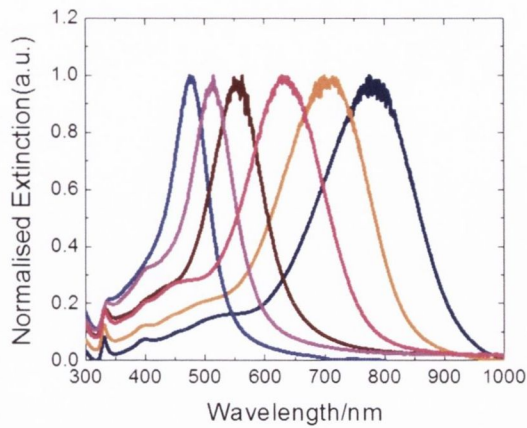
The LSP provided by the Au NP monolayer is observed to enhance the energy transfer in acceptor QD monolayer and donor QD monolayer where at the same distance between donor and acceptor monolayers, no apparent energy transfer in the absence of the LSP. The enhancement is examined with varying the Au NP concentration, Au NP-donor layer distance as well as Au NP-acceptor QD layer distance.

The LSP mediated energy transfer efficiency, rate or Förster radius increases with the Au NP concentration. It is found that the extended energy transfer range, in comparison with conventional FRET, can be described by an increase in the effective Förster radius in the presence of metal NPs. The range of the LSP coupled FRET can be tuned by varying the Au NP concentration. The acceptor emission also depends on the Au NP concentration but the maximum acceptor QD emission is not obtained at the highest Au NP concentration but the intermediate one. The acceptor emission is determined by the two competing process. LSP enhanced energy transfer contributes to the emission enhancement while the energy transfer from acceptor QDs to Au NPs results in the emission quenching.

The LSP mediated FRET efficiency or rate still follows a d^{-4} donor acceptor distance dependence for the planar geometry, which is similar as FRET or dipole-dipole behavior. But LSP mediated FRET is more sensitive on donor-Au NP layer separation than acceptor-Au layer separation. A fixed Förster radius for the varying acceptor QD-Au NP layer separation indicates that the strongly coupled donor-plasmon can be regarded as an enhanced donor dipole. The theoretical study is proved valid in the experimental data, the further study also demonstrates that greater enhancement of the LSP coupled FRET efficiency is achieved for preferential donor-plasmon coupling compared with acceptor-plasmon coupling.

This work is presented in Chapter 5, The distance dependent LSP coupled FRET has potential for a long range spectroscopic ruler or sensing applications. The emission changes in LSP mediated FRET system can be used in light emitting diodes applications.

Looking forward, it would be interesting to study the LSP coupled FRET by tuning LSP absorption peak wavelengths. Easily tunable silver prism is a good choice. As can be seen in Fig. 7.1, the colloidal silver prisms has the LSP absorption peaks covering the whole visible



λ_{Ext}/nm	Edge length/nm
477	9.3
512	14.9
555	21.8
633	34.2
704	45.6
782	58.0

Fig. 7.1 The silver prisms prepared following the approach in Ref.[206]. The thickness is (5.0 ± 0.4) nm

range by only changing the edge length. All these prisms have a thickness of $\sim (5.5 \pm 0.4)$ nm.

Localised Surface Plasmon in Quantum Well Pumping Quantum Dots

Based on the idea of LSP enhanced FRET in QDs systems, we propose and demonstrate a new approach to overcome the limited QW pumping QDs range through the LSP coupled FRET in QW-Au NP-QD hybrid structure. With the aid of LSP, a ~ 1.9 fold enhancement of R_0 is obtained, which greatly extends the QW-QD interaction range as a FRET pair. It makes it possible for the QW pumping QDs through nonradiative energy transfer over longer distances. Furthermore, a ~ 1.47 fold QD emission enhancement is obtained, which may enable the applications in QW-QD based color converters or light emitting diodes overcoming design issues related to the limited energy transfer distances.

Looking forward, it is only the first step in the development of QW-QD based device

with optimized conditions. It would be interesting to optimize the LSP coupled FRET in QW-QD systems through a systematic study.

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Appendix A

Optical Properties of QD solution

In this part, the absorption and PL spectra of all QD solutions used in this thesis are listed, the absorption peak, emission peak, FWHM, stokes shift, average QD size, quantum yield, the concentration of the solution are given for each one.

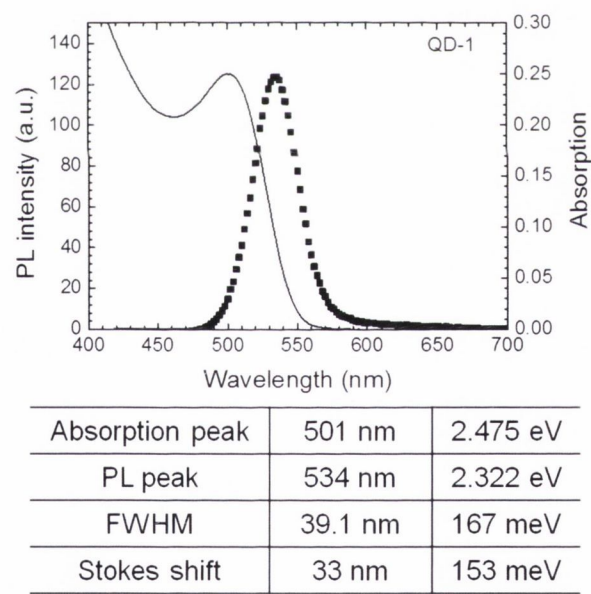


Fig. A.1 PL (squares, left-hand axis) and absorption spectra (line, right-hand axis) of QD-1 solution with $C_{Sol} = 5.25 \times 10^{-6}$ M. QD-1 has an average diameter of $D_{QD} = 2.55$ nm, the QY of QD-1 solution is $\Phi_{Sol} = 14\%$.

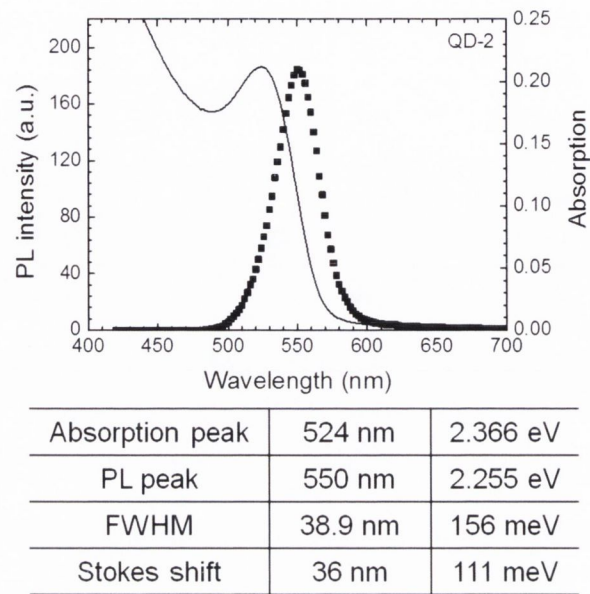


Fig. A.2 PL (squares, left-hand axis) and absorption spectra (line, right-hand axis) of QD-2 solution with $C_{Sol} = 2.98 \times 10^{-6}$ M. QD-2 has an average diameter of $D_{QD} = 2.6$ nm, the QY of QD-2 solution is $\Phi_{Sol} = 19\%$.

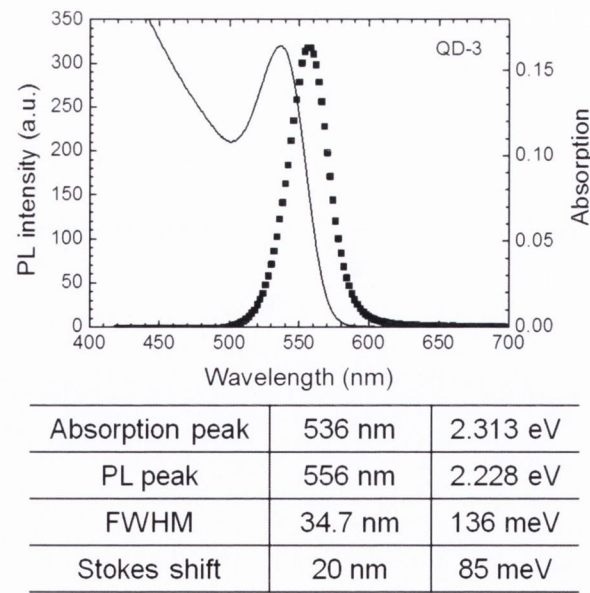


Fig. A.3 PL (squares, left-hand axis) and absorption spectra (line, right-hand axis) of QD-3 solution with $C_{Sol} = 1.82 \times 10^{-6}$ M. QD-3 has an average diameter of $D_{QD} = 3.1$ nm, the QY of QD-3 solution is $\Phi_{Sol} = 43\%$.

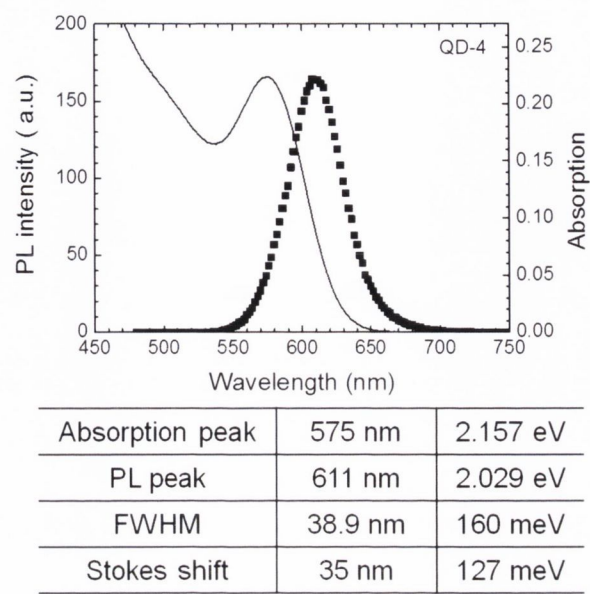


Fig. A.4 PL (squares, left-hand axis) and absorption spectra (line, right-hand axis) of QD-4 solution with $C_{Sol} = 2.15 \times 10^{-6}$ M. QD-4 has an average diameter of $D_{QD} = 3.3$ nm, the QY of QD-4 solution is $\Phi_{Sol} = 12\%$.

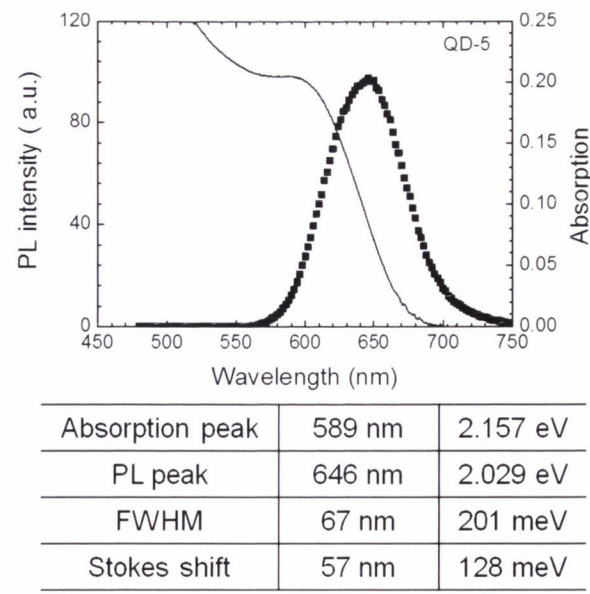


Fig. A.5 PL (squares, left-hand axis) and absorption spectra (line, right-hand axis) of QD-5 solution with $C_{Sol} = 3.15 \times 10^{-6}$ M. QD-5 has an average diameter of $D_{QD} = 3.4$ nm, the QY of QD-5 solution is $\Phi_{Sol} = 6\%$.

Appendix B

FRET and NSET Derivations for Bilayer

For a donor and an Au NP monolayer with concentration C_{Au} as shown in Fig B.1, FRET and NSET theories are derived from that for a single donor-Au NP pair. In FRET theory, an Au NP is treated as a dipole, the minimum distance of the donor and acceptor is centre-to-centre distance d_i . In NSET theory, an Au NP is treated as a nano surface, the distance of the donor and acceptor is from the centre of the donor to the Au surface, which is $d_i - r_{Au}$.

B.1 FRET Theory for Bilayer

For a donor and an Au NP monolayer with concentration C_{Au} shown in Fig B.1, FRET rate can be calculated by summing over all energy transfer rates in the acceptor layer as

$$\begin{aligned} k_{\text{FRET}} &= \sum_i k_i \\ &= \frac{1}{\tau_D} \sum_i \left(\frac{R_0}{d_i} \right)^6 \\ &= \frac{1}{\tau_D} \int_0^\infty \left(\frac{R_0}{d_i} \right)^6 \cdot C_{Au} \cdot dS_i \end{aligned} \tag{B.1}$$

while $d_i^2 = a^2 + d^2$, d is the minimum centre-to-centre distance of a donor dipole and the acceptor layer. a is shown in Fig. B.1. $N = C_{Au} \cdot dS_i = C_{Au} \cdot 2\pi a \cdot da$ is the number of all acceptor dipoles in the acceptor layer which have the same separation d_i with donor dipole,

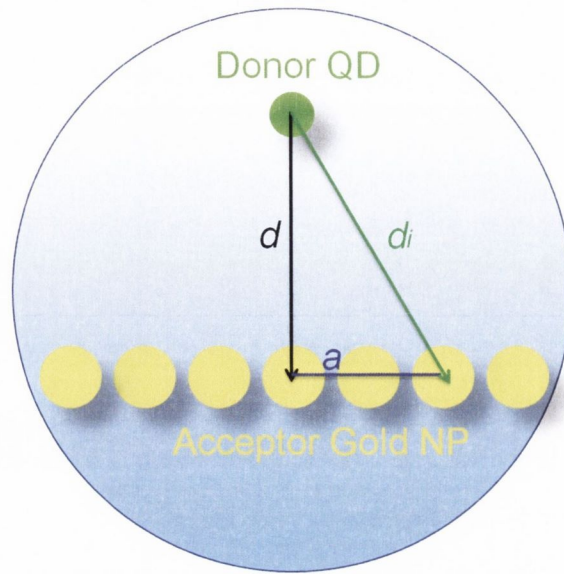


Fig. B.1 Cartoon of donor dipole interaction with a layer of acceptor Au NPs where a Au NP is regarded as a dipole or a surface, If an Au NP is treated as dipole, the QD-Au distance is d_i , the minimum QD-Au distance is $d = t + r_{QD} + r_{Au}$; if an Au NP is treated as a nano surface, the QD-Au distance is $d_i - r_{Au}$, the minimum QD-Au distance is $d - r_{Au}$.

it yields

$$\begin{aligned}
 k_{\text{FRET}} &= \frac{1}{\tau_D} \int_0^\infty \frac{R_0^6}{(a^2 + d^2)^3} \cdot C_{Au} \cdot (2\pi a \cdot da) \\
 &= \frac{1}{\tau_D} \int_0^\infty \frac{R_0^6}{(a^2 + d^2)^3} \cdot C_{Au} \pi \cdot d(a^2 + d^2) \\
 &= \frac{C_{Au} \pi R_0^6}{2d^4 \tau_D}
 \end{aligned} \tag{B.2}$$

The energy transfer efficiency is

$$\begin{aligned}
 E_{\text{FRET}} &= \frac{k_{\text{FRET}}}{k_{\text{FRET}} + k_r + k_{nr}} \\
 &= \frac{k_{\text{FRET}}}{k_{\text{FRET}} + \tau_D^{-1}} \\
 &= \frac{1}{1 + \frac{2d^4}{C_{Au} \pi R_0^6}}
 \end{aligned} \tag{B.3}$$

B.2 NSET Theory for Bilayer

For a donor and a layer of Au NPs with concentration C_{Au} as shown in Fig B.1, NSET rate could be extended by summing over all rates in the acceptor layer as

$$\begin{aligned}
 k_{\text{NSET}} &= \sum_i k_i \\
 &= \sum_i \left(\frac{d_0}{d_i - r_{Au}} \right)^4 \cdot C_{Au} \cdot dS_i \\
 &= \int_0^\infty \left(\frac{d_0}{d_i - r_{Au}} \right)^4 \cdot C_{Au} \cdot dS_i
 \end{aligned} \tag{B.4}$$

where similarly, $d_i^2 = a^2 + d^2$, d is the minimum centre-to-centre distance of a donor dipole and the Au NP monolayer $N = C_{Au} \cdot dS_i = C_{Au} \cdot 2\pi a \cdot da$, is the number of all acceptor Au NPs in the Au NP layer which have the same separation $d_i - r_{Au}$ with donor dipole

$$\begin{aligned}
 k_{\text{NSET}} &= \frac{1}{\tau_D} \int_0^\infty \left(\frac{d_0}{\sqrt{d^2 + a^2} - r_{Au}} \right)^4 C_{Au} (2\pi a \cdot da) \\
 &= \frac{1}{\tau_D} C_{Au} 2\pi d_0^4 \int_0^\infty \left(\frac{1}{\sqrt{d^2 + a^2} - r_{Au}} \right)^4 a da
 \end{aligned} \tag{B.5}$$

Suppose $y = \sqrt{d^2 + a^2}$,

$$\begin{aligned}
 &\int_0^\infty \left(\frac{1}{\sqrt{d^2 + a^2} - r_{Au}} \right)^4 a da \\
 &= \frac{1}{2} \int_0^\infty \left(\frac{1}{\sqrt{d^2 + a^2} - r_{Au}} \right)^4 d(d^2 + a^2) \\
 &= \frac{1}{2} \int_0^\infty \left(\frac{1}{y - r_{Au}} \right)^4 d(y^2) \\
 &= \int_d^\infty \left(\frac{1}{y - r_{Au}} \right)^4 y dy \\
 &= \int_0^\infty \left(\frac{1}{y - r_{Au}} \right)^4 (y - r_{Au} + r_{Au}) dy \\
 &= \int_0^\infty \left(\frac{1}{y - r_{Au}} \right)^3 dy + \int_0^\infty \left(\frac{1}{y - r_{Au}} \right)^4 r_{Au} dy \\
 &= \frac{1}{2(d - r_{Au})^2} + \frac{r_{Au}}{3(d - r_{Au})^3} \\
 &= \frac{3d - r_{Au}}{6(d - r_{Au})^3}
 \end{aligned} \tag{B.6}$$

Therefore,

$$\begin{aligned}
 k_{\text{NSET}} &= \tau_D^{-1} C_{Au} 2\pi d_0^4 \frac{3d - r_{Au}}{6(d - r_{Au})^3} \\
 &= \frac{3d - r_{Au}}{3(d - r_{Au})^3} \tau_D^{-1} C_{Au} \pi d_0^4
 \end{aligned}
 \tag{B.7}$$

The energy transfer efficiency is

$$\begin{aligned}
 E_{\text{NSET}} &= \frac{k_{\text{NSET}}}{k_{\text{NSET}} + \tau_D^{-1}} \\
 &= \left[1 + \frac{3(d - r_{Au})^3}{C_{Au} \pi d_0^4 (3d - r_{Au})} \right]^{-1}
 \end{aligned}
 \tag{B.8}$$

