Electrical and Optical Characterization of Colloidal Silicon Nanocrystals

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Dedication

This thesis is dedicated to my parents, Muqin Li and Yaorong Li, for their endless love of supporting me, believing in me, and teaching me the spirit of diligence and perseverance during my life.

Abstract

Colloidal silicon nanocrystals (SiNCs), due to their high photoluminescence efficiency and tunable bandgap, can be used to fabricate highly efficient hybrid nanocrystal-organic light-emitting-devices (NC-OLEDs) that emit in red or near infrared spectrum. Despite reports of outstanding device performance, the underlying mechanism of this high efficiency remains unknown. Consequently, this thesis focuses on studying the electrical and optical properties of SiNCs. The electrical conductivity and mobility of electrons and holes are successfully extracted in order to explain the observed dependence of device efficiency on SiNC surface ligand coverage. Steady-state and transient photoluminescence is also examined to better understand the connection between surface ligand coverage and molecular photophysics. In addition, these measurements are used to better understand the mechanisms for non-radiative exciton decay in SiNCs. This work elucidates the relationship between SiNC properties and device performance, potentially guiding the design of future NC materials for high performance.

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Chapter 1 Introduction to Semiconductor Nanocrystals

1.1 Introduction

Nanocrystals (NCs) or quantum dots (QDs) usually refer to tiny crystals consisting of hundreds to a few thousand atoms, with size ranging from 2 to about 20 nm. Typically, when crystal size falls into this regime, quantum mechanical confinement can significantly modify the electronic band structure [1-10]. This opens interesting possibilities to tailor the electrical or optical behavior of a material without changing its chemical composition. For example, by varying the size of NCs, the resulting energy band gap can be easily tuned [3, 11-18].

Inorganic semiconductors are often characterized by superior charge carrier mobilities, photo- and thermal-stability, permitting their integration into high performance electrical and optoelectronic devices [19]. Despite their many attractive features and demonstrated high device performance, device fabrication is often costly due to the use of high temperatures and a difficulty in increasing processing throughput. The latter is complicated in part by the fact that these are often mechanically hard materials that are not compatible with flexible plastic or foil substrates.

Colloidal semiconductor NCs could offer a cost-effective solution to balance the need for high performance with ease-of-processing. Since colloidal NCs form thermodynamically stable solutions, solution-based fabrication process including spin-coating or dip-coating, in addition to conventional large-area coating techniques can be exploited [19-24]. As such, nanomaterials have been recognized as potential building blocks for low cost and large-scale electronic or optoelectronic devices [19, 25-28].

The potential applications for NCs are broad, including photovoltaic cells (PVs) [22, 24, 29-32] and light-emitting devices (LEDs) [21, 33-43]. The tunable electronic band structure [1] and high photoluminescence efficiency [3] makes NCs promising in these areas. In addition, due to their solution processablity [44], it is possible to integrate NCs with other novel materials such as organic semiconductors [21, 33-37, 43, 45-49], carbon nanotubes [50-54] or nanowires [55-58] into a hybrid device to further harness the advantage that NCs possess.

1.2 Scope of This Thesis

The main goal of this thesis is to explore the various parameters responsible for the observation of high external quantum efficiency in hybrid silicon nanocrystal-organic light-emitting devices (Si NC-OLEDs). The rest of this chapter is devoted to introducing the basics of nanocrystals, with focus particular focus on silicon nanocrystals (SiNCs). Chapter 2 will discuss the theory and recent progress in NC-OLEDs. Chapter 3 will illustrate the experimental methods used in this thesis. Chapter 4 will discuss the electrical properties of SiNCs, while Chapter 5 will explore the mechanisms for photoluminescence (PL) in SiNCs. Chapter 6 will offer conclusions for this thesis and propose future research directions.

1.3 Introduction to Silicon Nanocrystals

The synthesis of colloidal NCs was first reported in 1993 by Murray et al. [3]. They mixed a hydrophobic solution containing Cd with another that had either S, Se or Te

element at high temperature. Followed with rapid quenching, nanocrystals formed, which would then be quickly passivated by surfactants and became stable in solution. Due to the ease of their chemical synthesis and the excellence of their optical properties (PL efficiency, η_{PL}~80%), Group II-VI NCs, such as CdSe [47, 51, 58-65], are considered as the most popular NCs in research.

The research on colloidal SiNCs, however, is less developed as compared with CdSe NCs. This is mainly due to a very low PL efficiency (<0.1%) in the bulk form [66]. Additionally, despite of its good electrical performance, the study of luminescence from Si is complicated by the fact that it is an indirect bandgap material [67]. As a result, the external quantum efficiency of bulk Si based LEDs is typically low.

Silicon nanocrystals (SiNCs) can offer a route around the issues related to the indirect bandgap of silicon. Quantum confinement in SiNCs can supply "momentum conservation" phonons that significantly improve their PL efficiency up to ~60% [2, 18, 68, 69]. Additionally through precise control on crystal size during the synthesis step [18], tunable emission color by SiNCs could also be experimentally achieved (Figure 1). Additionally, compared with CdSe NCs, SiNCs are considered earth abundant and lower in toxicity, which is desirable for large-scale production. These attributes make SiNCs a promising material for application in LEDs.

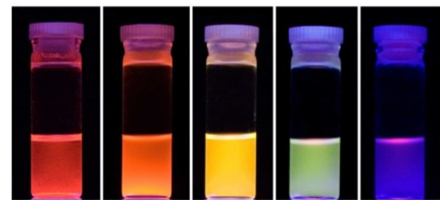

Figure 1.1 Photographs of deep red (740 nm), red (675 nm), yellow (592 nm), green (572 nm) and blue (441 nm) photoluminescence from SiNCs, pumped at a wavelength of 365 nm. (Reprinted from [18])

Beyond offering a new active material for semiconductor devices, the study of SiNCs may also benefit the whole semiconductor industry.

Currently, electronic circuits in 22 nm channel length have already been used for commercial applications, with 14 nm technologies under development in laboratories [70]. Due to similarities in feature size, knowledge obtained from studying colloidal SiNCs could help in understanding design rules for next generation electronic circuits.

1.4 Quantum Confinement in Nanocrystals

1.4.1 Introduction to Quantum Confinement Effect

Size dependent quantum confinement effects begin to modify the bandgap of NCs when their size reaches a critical value, or Bohr radius, which is defined as [71]:

$$a_B = \varepsilon_r \frac{m}{m^*} a_0 \tag{1.1}$$

where ε_r is the dielectric constant of the NC, m^* is the effective mass of the electron in the NC, m is the electron rest mass, and a_0 is the Bohr radius of the Hydrogen atom. For CdSe and Si, the Bohr radius are ~60 Å [71] and ~50 Å [72, 73], respectively.

When the NC size falls below its Bohr radius, an exciton, or a bounded electron-hole pair, will experience quantum confinement by the physical crystal boundaries. This will also force the energy bands to split into discrete levels, resulting in a quantized distribution in density of states (the number of states per energy interval per volume that could be occupied by electrons or holes), as shown in Figure 1.2 [67, 74, 75].

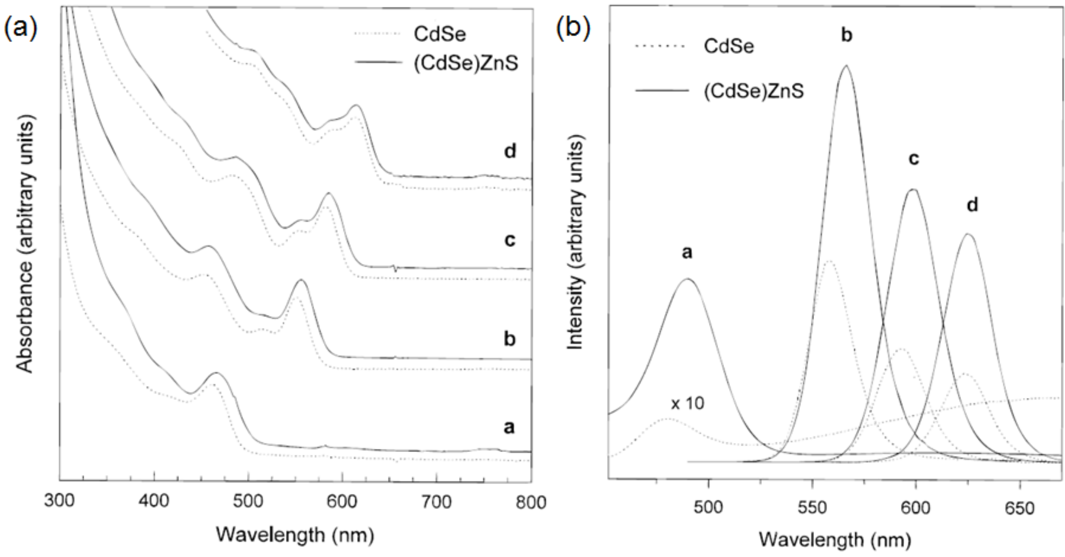

Figure 1.2 Room temperature size-dependent absorption **(a)** and photoluminescence **(b)** spectra of CdSe NCs (dashed line) and Zinc Sulfide (ZnS) coated CdSe NCs (solid line). The curve **a** refers to particles with average diameter 23 Å, curve **b**: 42 Å, curve **c**: 48 Å, and curve **d**: 55 Å. (Reprinted from [65])

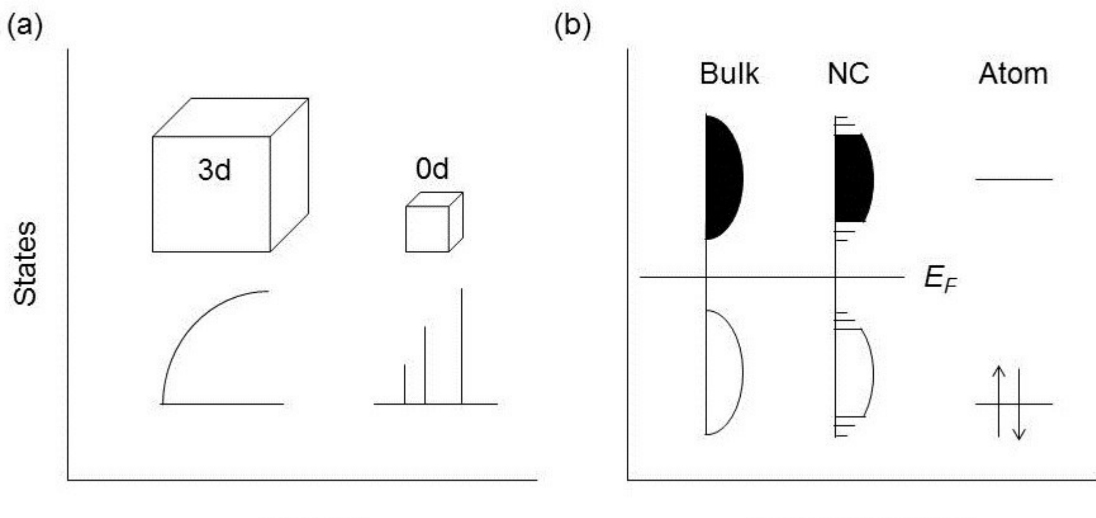

Figure 1.3 Density of states of a semiconductor: **(a)** Comparison of idealized density of states for one band of a semiconductor in 3-dimensions (3d) and in 0-dimension (0d), with 3d bulk materials showing a continuous density of states and 0d case show a molecular-like (or discrete) density of states; **(b)** The change of density of states from bulk to nanocrystal, and then to atomic limit. Note that the energy band gap between the valence band (VB) and conduction band (CB) increases with decreasing size in the material. The open region and solid region stands for occupied and unoccupied states, respectively. E_F represents the level of Fermi energy.

1.4.2 Quantum Mechanical Model of Confinement

For simplicity, the quantum confinement of a single carrier is often described by the particle-in-a-box model, in which the motion of the electron (or hole) is given by Schrödinger's equation:

$$H\psi = E\psi \tag{1.2}$$

where H is Hamiltonian operator, ψ is the wavefunction and E is the energy of the carrier. Taking the effective mass approximation proposed by Brus [1], the Hamiltonian of a single-charge spherical nanoparticle with a radius R and with infinite external potential barrier can be written as following:

$$H = \frac{h^2}{8\pi^2 m^*}\nabla_r^2 + V,\ V = 0 \text{ when } r<R \text{ and } V=\infty \text{ when } r\geq R \tag{1.3}$$

where h is Planck's constant and r is the distance from the center of the particle. The solution to Equation (1.3) gives:

$$\psi_n(r) = \frac{1}{r\sqrt{2\pi R}} sin(\frac{n\pi r}{R}) \tag{1.4}$$

$$E_n = \frac{h^2 n^2}{8m^* R^2} \tag{1.5}$$

Equations (1.4) and (1.5) reveal the behavior of an electron within an infinite potential barrier and also qualitatively describe the observed blue shift in bandgap with shrinking size.

In an excited nanocrystal where both electron and hole exist, the analytical form of H becomes complicated. In addition to the kinetic energy term, the Coulomb interaction between the electron and hole (V_c), and polarization at the NC surface (V_p) should also be taken into account [76]. The expression for H is modified as:

$$H = \frac{h^2}{8\pi^2 m_e}\nabla_e^2 + \frac{h^2}{8\pi^2 m_h}\nabla_h^2 + V_c + V_p \tag{1.7}$$

In which:

$$V_c = -\frac{e^2}{4\pi\varepsilon_1|\vec{r_e}-\vec{r_h}|} \tag{1.8}$$

$$V_p = \frac{e^2}{2}\sum_{n=1}^{\infty}\alpha_n \frac{(|\vec{r_e}|)^{2n}+(|\vec{r_h}|)^{2n}}{R^{2n+1}} \tag{1.9}$$

$$\alpha_n = \frac{(\frac{\varepsilon_1}{\varepsilon_2}-1)(n+1)}{\varepsilon_1(\frac{n\varepsilon_1}{\varepsilon_2}+n+1)} \tag{1.10}$$

Here e and h stand for electron and hole, respectively. V_c and V_p are both functions of electron and hole position (r_e and r_h, refer to Figure 1.4) and ε_1 and ε_2 is the dielectric constant of the NC and the surrounding medium, respectively. Assuming that the electron and hole wavefunctions are uncorrelated, and that the radius R is small, the solution to Equation (1.2) is:

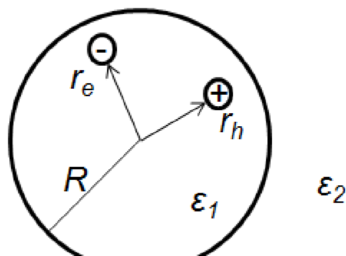

Figure 1.4 Schematic of a spherical NC with dielectric constant ε_1 embedded in a material with dielectric constant ε_2.

$$E = E_{g,bulk} + E_{ex} \approx E_{g,bulk} + \frac{h^2}{8R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) \tag{1.11}$$

The sum of the kinetic energy of the electron and hole is approximately taken as the internal energy of the exciton, which adds up to the total energy bandgap of a semiconductor material. From Equation (1.11), the smaller the nanocrystal radius R, the larger the bandgap, as shown in Figure 1.3, when R decreases toward the atomic limit. The experimental observed bandgap reveals a good match with the approximation from Equation (1.11) when the size of nanocrystal is greater than 8 nm, as shown in Figure 1.5.

1.5 Charge Carrier Transport in Nanocrystals

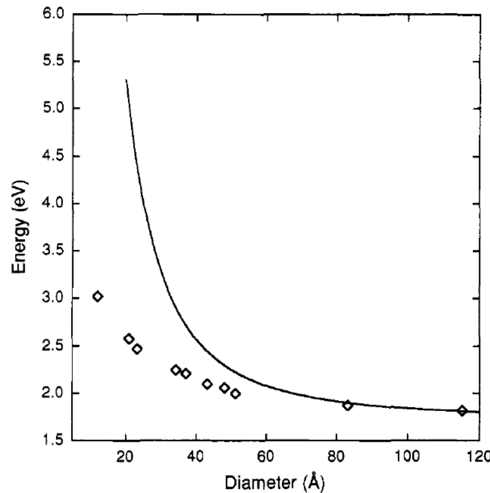

Figure 1.5 Comparison of the calculated value of the bandgap using the effective mass approximation (solid line) to experimental data (open diamonds) for CdSe NCs. (Reprinted from [3])

Charge injection in semiconductors often depends on the Fermi energy difference between the semiconductor and an injecting metal contact. Ohmic contact for electron transport requires that the Fermi energy (work function) of metal be smaller than the Fermi energy of the semiconductor, which at the same time, also serves as a Schottky barrier for holes. This effect can be used to separate electron and hole transport. Electron-only and hole-only SiNC devices can be made by referring to the energy band diagram in Figure 1.6, allowing electron mobility (μ_h) and hole mobility (μ_e) to be decoupled. For simplicity, energy band bending in the device is ignored and not plotted in the figure.

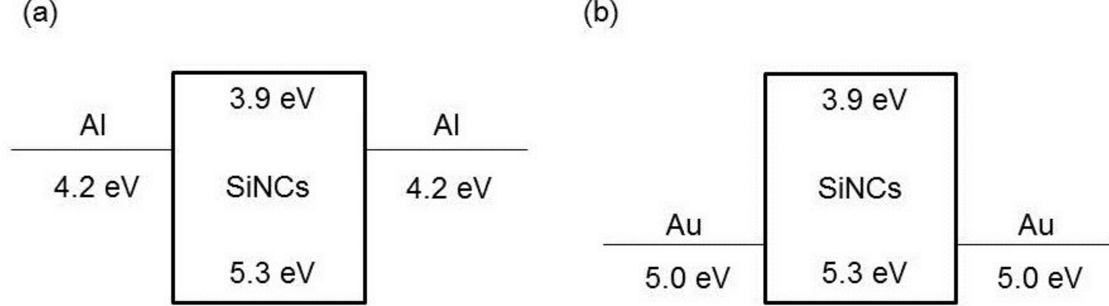

Figure 1.6 Energy band diagram for **(a)** an electron only device and **(b)** a hole only device.

Due to the quantum confinement effect, the valence band (VB) and conduction band (CB) energies for the SiNCs are estimated by correcting those of bulk silicon. The

electroluminescence spectrum of 5 nm SiNCs peaks at ~868 nm (1.43 eV) [77], giving a confinement energy ~0.3 eV. Of the total confinement energy, 0.2 eV is assigned to the VB, and 0.1 eV is assigned to the CB [14].

Suppose the electron and hole densities are n_e and n_h, respectively, the conductivity σ in SiNCs can be expressed as in Equation (1.12).

$$\sigma = n_e e\mu_e + n_h e\mu_h \tag{1.12}$$

Take electron transport as an example. Electrons in excess of thermal equilibrium density n_e can be injected through Ohmic cathode when the carrier transient time is less than the field-free dielectric relaxation time [78]. This can be viewed as a threshold voltage above which the injected electron density n exceeds n_e. This threshold is given by Equation (1.13), where e is elementary charge, d is the device thickness and ε is the dielectric constant of the semiconductor:

$$V_i = \frac{n_e e d^2}{2\varepsilon} \tag{1.13}$$

Below V_i, the current density J_Ω follows Ohm's law and is linearly proportional to voltage V, as shown in Equation (1.14). While above V_i, if there is no trap present, J_C is limited by the space-charge of injected electrons and follows Equation (1.15) (Mott-Gurney law). This regime ($J \propto V^2$) is often known as space-charge limited conduction (SCLC).

$$J_\Omega = n_e e\mu_e \frac{V}{d} \tag{1.14}$$

$$J_c = \frac{9}{8}\mu_e \varepsilon \frac{V^2}{d^3} \tag{1.15}$$

If traps are present, most of the injected electrons will be localized and not contribute to current flow. This situation applies when $n_e<n<n_t$, where n_t is the trap density. Assuming

the trap energies are energetically exponentially distributed in the band gap, the density of traps per unit energy $n_t(E)$ will follow Equation (1.16), in which N_c and E_c are the density of states and energy of conduction band, k_B is the Boltzmann's constant and T_t is the characteristic temperature of traps. The current density J_t in this regime is found to be proportional to V^{l+1}, where $l=T/T_t$, as shown in Equation (1.17).

$$n_t(E) = \frac{n_t}{k_B T} \exp\left(\frac{E-E_c}{k_B T}\right) \tag{1.16}$$

$$J_t = N_c \mu_e e^{1-l} \left(\frac{\varepsilon l}{n_t(l+1)}\right)^l \left(\frac{2l}{l+1}\right)^{l+1} \frac{V^{l+1}}{d^{2l+1}} \tag{1.17}$$

For instance, for CdSe NC thin film samples [59], the current has a linear dependence on voltage at low field. As the injected current increases, trap-limited space charge conduction takes place. The transition voltage V_Ω is given by Equation (1.18) and indicated by the arrow in Figure 1.7. When n is further increased to be greater than n_t, J-V relation will fall back to V^2 dependence and enter SCLC regime, illustrated by the top region of the 30 nm sample in Figure 1.7. The transition voltage V_c between these two regimes is given by Equation (1.19).

$$V_\Omega \approx \left[\frac{n_e}{N_c}\right]^{\frac{1}{l}} \left[\frac{e n_t d^2}{\varepsilon}\right]^{l+1} \tag{1.18}$$

$$V_c \approx \frac{ed^2}{\varepsilon} \left[\frac{9}{8} \frac{n_t^l}{N_c} \left(\frac{l+1}{l}\right)^l \left(\frac{l+1}{2l+1}\right)^{l+1}\right]^{\frac{1}{l-1}} \tag{1.19}$$

In disordered systems (for example, NC thin films), a field dependent mobility is often observed due to a drop in the potential barrier height ΔU for conduction when an electrical field F is present. Assuming the semiconductor simply is a system of neutral atoms, the potential change when an electron is ionized to a distance r from nucleus can be thought as the combination of Coulomb force from nucleus and from electrical field,

as shown in Equation (1.20) [79]. The maximum of ΔU is found when these two terms equal, which gives the expression in Equation (1.21). Conduction is simply considered as a thermally activated process, thus the expression for mobility can be written as in Equation (1.22), where μ_0 is zero field mobility and α (Equation (1.23)) is named as Poole-Frenkel coefficient. Taking this field-dependent mobility into account, we can have Equation (1.24) for the current density J_Ω in Ohmic regime.

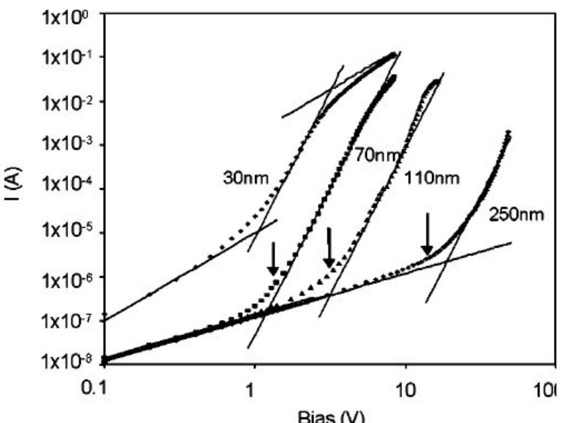

Figure 1.7 Current-voltage characteristics for CdSe NC devices with a variable thickness of CdSe. Solid lines are fits to the theoretical models. Arrows indicate calculated values for V_Ω. (Reprinted from [59])

$$\Delta U = eFr + \frac{e^2}{4\pi\varepsilon r} \tag{1.20}$$

$$\Delta U_m = \sqrt{\frac{e^3 F}{\pi\varepsilon}} \tag{1.21}$$

$$\mu(F) = \mu_0 \exp\left(-\frac{\Delta U_m}{k_B T}\right) = \mu_0 exp(-\alpha\sqrt{F}) \tag{1.22}$$

$$\alpha = \frac{e}{k_B T}\sqrt{\frac{e}{\pi\varepsilon}} \tag{1.23}$$

$$J_\Omega = n_e e \mu_0 F exp(-\alpha\sqrt{F}) \tag{1.24}$$

These equations allow us to calculate the mobilities of electron and hole though *J-V* measurement. Further discussions will be included in Chapter 4.

1.6 Exciton Generation and Recombination in Nanocrystals

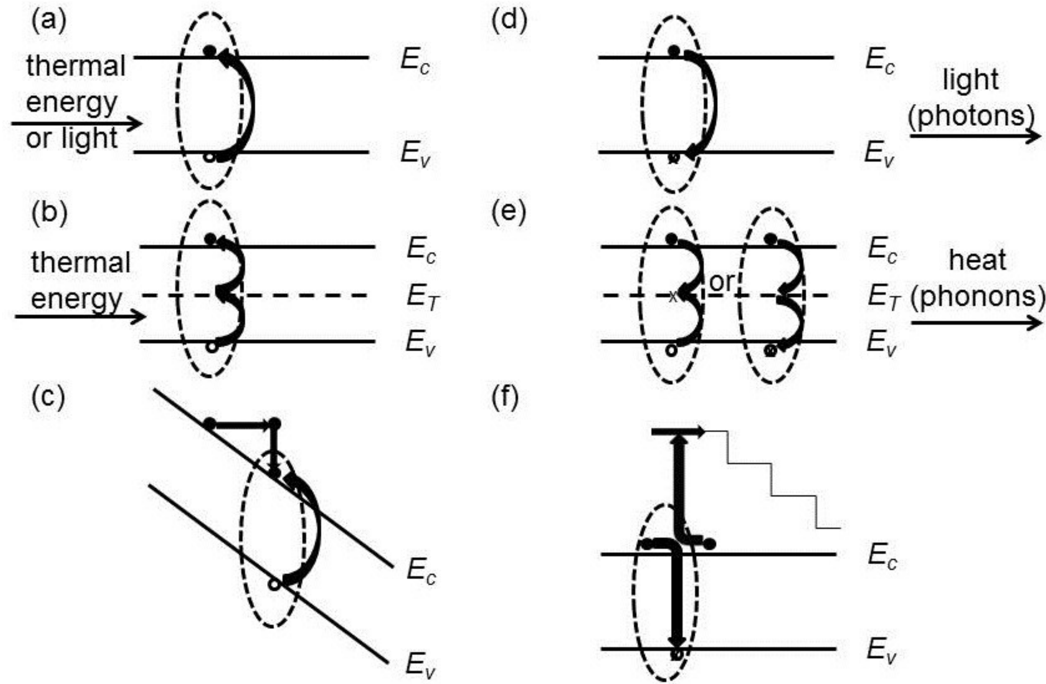

Figure 1.8 Visualization of generation events via **(a)** band-to-band **(b)** R-G center **(c)** impact ionization processes and recombination events via **(d)** band-to-band **(e)** R-G center **(f)** Auger processes. Solid dot and open dot represent electrons and holes, respectively. Dashed ellipses represent excitons. E_c and E_v stand for the energy of conduction band (CB) and valence band (VB). E_T corresponds to mid-gap trap energy level. x marks a recombination event.

A schematic plot of exciton generation and recombination processes is shown in Figure 1.8. In a bulk semiconductor, an exciton can be formed via: (a) band-to-band generation, in which either thermal energy or light is absorbed to promote an electron from the VB to the CB; (b) Recombination-Generation (R-G) center generation (also referred as Shockley-Read-Hall (SRH) generation), in which thermally assisted generation with an R-G center acting as an intermediary; or (c) impact ionization, which requires a very high electrical field. The recombination process can be thought as the reverse of generation process: (d) band-to-band recombination may lead to photon

emission; (e) R-G center recombination (also referred as SRH recombination), on the other hand, is non-radiative and thus only heat (or phonon) is emitted; (f) Auger processes, which involve two particles (an exciton with a charge carrier, or sometimes two excitons), become likely only when the exciton concentration is high.

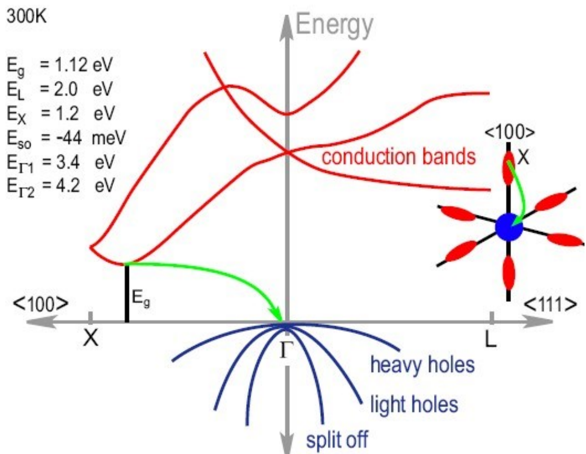

Figure 1.9 Room temperature energy band diagram of bulk Si. (Reprinted from [39])

In bulk Si, an indirect bandgap semiconductor, radiative band-to-band recombination is ineffective at room temperature. To have band-to-band recombination, a phonon must accompany the process to conserve the crystal momentum. This process is shown by the arrow in the energy band diagram of Si in Figure 1.9. As a result, nonradiative R-G recombination dominates the recombination process in bulk Si [80] and the η_{PL} is very low.

In SiNCs, however, η_{PL} can increase over orders of magnitude relative to bulk Si [18]. The definition of η_{PL} is shown in Equation (1.25), in which k_r (or $1/\tau_r$) is radiative recombination rate and k_{nr} (or $1/\tau_{nr}$) is the nonradiative recombination rate. The total decay rate k (or $1/\tau$) can be easily calculated using the sum of these two terms, as shown in Equation (1.26).

$$\eta_{PL} = \frac{k_r}{k_r + k_{nr}} \tag{1.25}$$

$$k = k_r + k_{nr} \tag{1.26}$$

The increase in η_{PL} in SiNCs compared to the bulk must come either from a decrease in k_{nr} and/or an increase in k_r. The former is likely due to the decrease of R-G centers, which dominate the non-radiative recombination process in bulk Si [80]. In nanocrystals that are small enough to show quantum confinement effects, as some authors argued [39], the R-G centers (midgap defects) are thermodynamically unfavorable and tend to grow out of the nanocrystal.

There are two factors that contribute to improvement in the radiative recombination rate k_r. First, the uncertainty in momentum space that quantum confinement introduces relaxes the momentum conservation rule and allows a greater proportion of the phonon to assist in the indirect band-to-band transition [81]. This effect is thought to be insufficient to make the bandgap of SiNCs direct but the optical transitions might possibly be described as less indirect or quasi-direct [68]. Second, because the nanocrystal forms a potential well that confines the electron and the hole spatially, their wavefunctions overlap more in position space, recombination events between electrons and holes become more likely to occur [2].

In most cases, exciton decay is characterized by Equation (1.27), where g is the exciton generation rate and n is the exciton concentration. When a pulsed laser source (< 1 ns in pulse width) is used, g becomes 0 at t>0. The solution gives a single exponential decay, as shown in Equation (1.28).

$$\frac{dn}{dt} = g - kn \tag{1.27}$$

$$n(t) = n_o exp(-kt) \tag{1.28}$$

If excitons are dominated by single exciton decay (without nonlinear terms), the PL intensity I is linearly proportional to exciton density n. It should however be noted that the recombination processes in SiNCs are likely more complicated. Surface recombination and Auger recombination, which are ignored in the previous discussion, may be even worse in SiNCs than in bulk. This is due to the higher surface-to-volume ratio and higher exciton concentration within the small nanocrystal volume [82]. In SiNCs, instead, stretched exponential decay fitting (Kohlrausch decay equation), is frequently used (Equation. (1.29)).

$$n(t) = n_o exp[-(kt)^{\beta}] \tag{1.29}$$

In this equation, an empirical fitting parameter β, sometimes named as dispersion coefficient, is used to explain the discrepancy from single exponential fitting (where β=1). The dispersion coefficient β is usually explained by lifetime distribution due to size variation in NCs [83] or exciton transfer between NCs [84]. To better understand the decay dynamics of excitons and the origin of photoluminescence in SiNCs, further study is thus needed. This will be discussed in detail in Chapter 5 in the thesis.

Chapter 2 Introduction to Hybrid Nanocrystal-Organic Light-Emitting Devices

2.1 Introduction

Light-emitting-device (LED) has emerged as a potential approach to save energy and alleviate global warming [85]. In such devices, the conversion efficiency from electricity to light emission is 5~6 times higher than incandescent light bulbs [85]. In addition, LEDs are also considered as longer in working lifetime, and lower in maintenance requirement. These attributes of LEDs could lead to a complete revolution in the lighting industry in the near future.

In history, LEDs were discovered more than 100 years ago [86]. Until recently, most research has focused on inorganic semiconductor LEDs, with the study of organic LEDs (OLEDs) only beginning in 1987 [87]. Recently, hybrid-material based LEDs, such as hybrid nanocrystal-organic light-emitting devices (NC-OLEDs) have gained in their interest due to the ease that the LED emission wavelength can be tuned through variations in NC size.

The first NC-OLED was demonstrated in 1994 using group II-VI CdSe NCs, and a conjugated polymer, poly-(para-phenylenevinylene) (PPV) [43]. Although the external quantum efficiency (η_{EQE}, photons out per electron in) of this device was only 0.001% [43], this work sparked new interest in the area of hybrid optoelectronic devices. To date, most work has focused on compound semiconductor NCs including group II-VI [21, 35, 43, 65, 88, 89], III-V [41], and IV-VI [49, 90]. Core-shell structured Group II-VI NCs were also utilized to help increase the device efficiency. Very recently, an impressive

external quantum efficiency of 18% was reported using CdSe/CdS (core/shell) NCs [35]. This was the first time for a hybrid NC-OLED reported with efficiency comparable to that of phosphorescent OLEDs [91]. In Table 2.1 progresses made in the last two decades on NC-OLEDs are briefly summarized.

Nanocrystals	Emission Wavelength	External Quantum Efficiency	Turn-on Voltage	Year
CdSe	580-620 nm	0.001-0.01%	~4 V	1994
CdSe/CdS	613 nm	0.22%	~4 V	1997
CdSe/ZnS	562 nm	0.52%	~4 V	2002
CdSe/ZnS	540-635 nm	>2%	-	2005
CdSe/ZnS	600 nm	2.7%	~2.5 V	2009
CdSe/ZnS	~610 nm	18%	~1.7 V	2013

Table 2.1 Summary of the progress of NC-OLEDs in the visible emission range.

In addition to displays and solid-state lighting in the visible spectrum, NCs also have the potential to be applied to the near infrared (NIR) and infrared for application in optical communications (1300 nm - 1500 nm) [15, 49, 90] and tissue imaging (800 nm - 1100 nm) [92-94]. CdSe NCs, due to the large bulk energy bandgap (1.74 eV, corresponds to ~710 nm), cannot emit in the near infrared spectrum. The tunability of frequently-seen semiconductors is shown in Figure 2.1. From this plot, group III-V [41] and group IV-VI NCs [15, 49, 90] are both good candidates for NIR emission. In fact, due to similarity in colloidal synthesis procedures, research interest in group IV-VI NCs, especially PbS and PbSe NCs has grown in recent years.

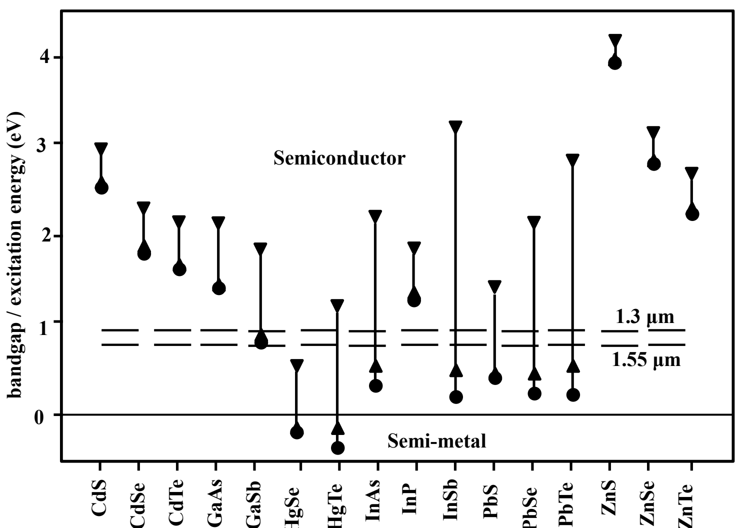

Figure 2.1 Tunable energy bandgap of NCs. The bandgap energies are calculated using a simple particle-in-a-box model [1]. Circles stand for the bandgap energies of bulk materials. Downward-pointing triangles show energies of 3 nm nanocrystals, and upward-pointing triangles show energies for nanocrystals at 10 nm. The optical communication window (1.3 µm to 1.5 µm) is also marked as reference. (Reprinted from [44])

In Table 2.2, progress in group III-V and group IV-VI NIR NC-OLEDs is summarized [38, 41, 46, 95]. Unlike visible emitting NC-OLEDs, their external quantum efficiencies are typically lower, with the maximum only at 2% [95]. Despite the slow improvement, the device efficiency still is still lags the requirements for commercialization. As such, new semiconductor materials are proposed to solve this issue, for instance, SiNCs [77]. This will be discussed in the next session.

Nanocrystals	Emission Wavelength	External Quantum Efficiency	Turn-on Voltage	Year
InAs/ZnSe	1300 nm	0.5%	15 V	2002
PbSe	1495 nm	0.001%	10 V	2003
PbS	1200 nm	1.15%	1 V	2008
PbS	1054 nm	2.0%	1.2 V	2012

Table 2.2 Summary of reported near-infrared-nanocrystal electroluminescence.

2.2 Operating Mechanism of Hybrid SiNC-OLEDs

Electroluminescence (EL) in nanostructured Si, or porous Si, was first discovered in early 1990s [96]. Field-effect EL in SiNCs was later demonstrated in 2005 [40]. Our group showed that a hybrid SiNC-organic LED (NC-OLED) can have an external quantum efficiency (η_{EQE}) of 0.6% in the NIR [77]. With careful choice of hole-transport material, device efficiency has been improved up to 8.6% [34], a record efficiency for NIR NC-OLEDs.

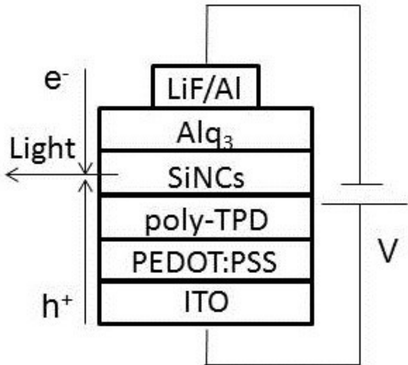

Figure 2.2 Structure of a hybrid Si NC-OLED. Indium tin oxide (ITO) is used as transparent anode, poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) as an injection layer (HIL), poly(4-butylphenyl-diphenyl-amine) (poly-TPD) as a hole transport layer (HTL), SiNCs as an emissive layer (EML), tris(8-hydroxyquinolinato) aluminum (Alq_3) as an electron transport layer (ETL) and lithium fluoride (LiF)/Al as the cathode.

A typical structure for a SiNC-OLED is shown in Figure 2.2. The SiNC-OLEDs are fabricated by sandwiching the inorganic NC emissive layer (EML) between organic charge transport layers. Detailed procedures can be found in [34]. Briefly, PEDOT:PSS and poly-TPD solution are spun-coated on clean ITO substrates. Followed with heat and UV treatment to stabilize these layers, SiNCs are then spun-coated on top. Finally, Alq_3 and Al are deposited using thermal evaporation, defining a device contact area of a circle in 1 mm diameter.

The energy band diagram of the Si NC-OLED with optimized efficiency is shown in Figure 2.3. As can be seen in this plot, when the ITO anode is forward biased with respect to the LiF/Al cathode, holes are injected from the ITO and electrons from Al. The

electrons and holes form excitons that are confined to the SiNC layer, which may then recombine radiatively and emit photons.

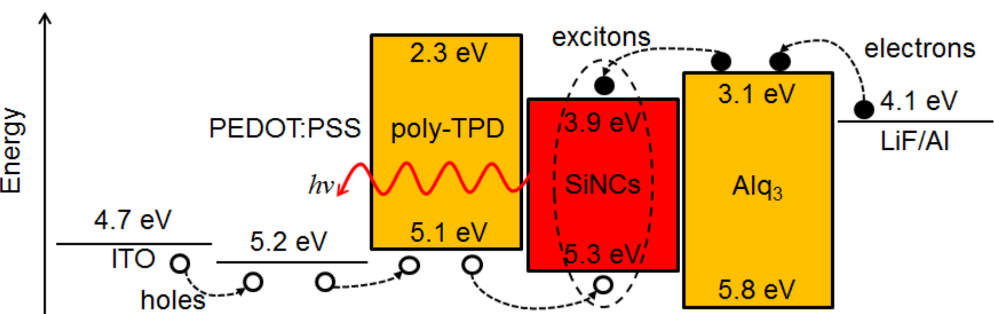

Figure 2.3 Energy band diagram of a Si NC-OLED, using 5 nm SiNCs. Open dots and solid dots stand for holes and electrons separately.

2.3 External Quantum Efficiency of Hybrid SiNC-OLEDs

The external quantum efficiency (η_{EQE}) is the ratio of forward-emitted photons per injected electron. Formally, the η_{EQE} is defined as:

$$\eta_{EQE} = \eta_{OC}\gamma\chi\eta_{PL} \quad (2.1)$$

where η_{OC} is the optical outcoupling efficiency, which is the fraction of internally generated photons that escape into the forward viewing direction (Figure 2.4). A significant portion of photons are indeed trapped inside the device due to total internal reflection (TIR) and waveguiding in the organic layers or in the substrate. Additionally, photons formed in the organic layer can also be quenched by the metal

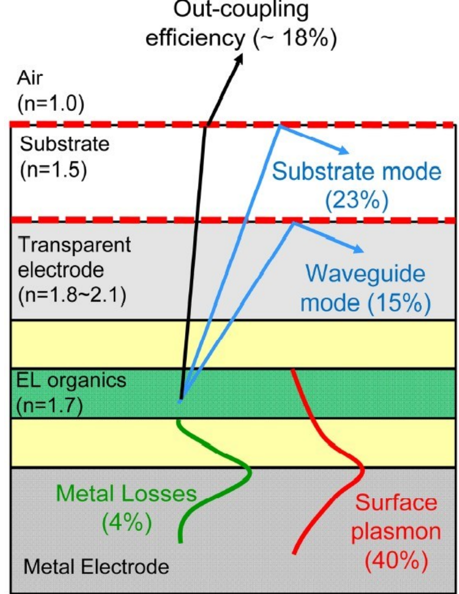

Figure 2.4 Various kinds of light out-coupling losses in OLEDs. (Reprinted from [97])

electrode. As a result, η_{OC} is typically <20% in OLEDs [97]. It should be noted that as the refractive index of SiNCs (n~3.5 in bulk form) and emission wavelength of SiNC-OLEDs are different from typical organics and OLEDs, the estimation is rough. However, a recently publication shows that infrared emitting PbSe (n~16 in bulk form) NC-OLED has a η_{OC}~20% at 1150 nm [98]. So for simplicity, we assume η_{OC} as 20% in our SiNC-OLEDs.

The charge balance factor, γ, is the fraction of injected carriers that actually form excitons in the EML. It is difficult to probe γ directly but it is generally believed that in state-of-art, high efficient OLEDs where mobilities of electrons and holes are well balanced and where blocking layers prevent leakage current, γ could reach unity.

The exciton spin fraction χ is defined as the ratio of singlet exciton states over the sum of singlet and triplet exciton states. A singlet exciton is formed when a ground state (a pair of electrons, with one spin up and another spin down) is optically excited. To conserve spin momentum, the electron in the excited state will have different spin direction compared to the ground state electron, resulting in net spin S=0 (Figure 2.5 (a)). However, if the exciton is formed via electrical excitation, each electron could have an independent electron spin orientation. This process can be visualized by using the vector model as shown in Figure 2.5, where the electron spin is treated as a rotating vector with an orbital momentum. The individual vectors represent the state of either spin up or spin down. If the two electrons have the same spin direction, a triplet state is formed, with a net spin S=1 (Figure 2.5 (b) to (d)). Simple spin statistics predicts that under electrical excitation there will be three times as many triplet excitons as there are singlet excitons

[99]. As a result, for a fluorescent OLED in which only singlets can radiatively emit, spin fraction χ equals 0.25. While in CdSe NCs, it has been argued that χ could be close to unity [35], spin statistics remains unclear in SiNCs. It is very unusual for a light atom such as Si to show phosphorescence at room temperature. If SiNCs could only fluoresce, the value of χ is also 0.25.

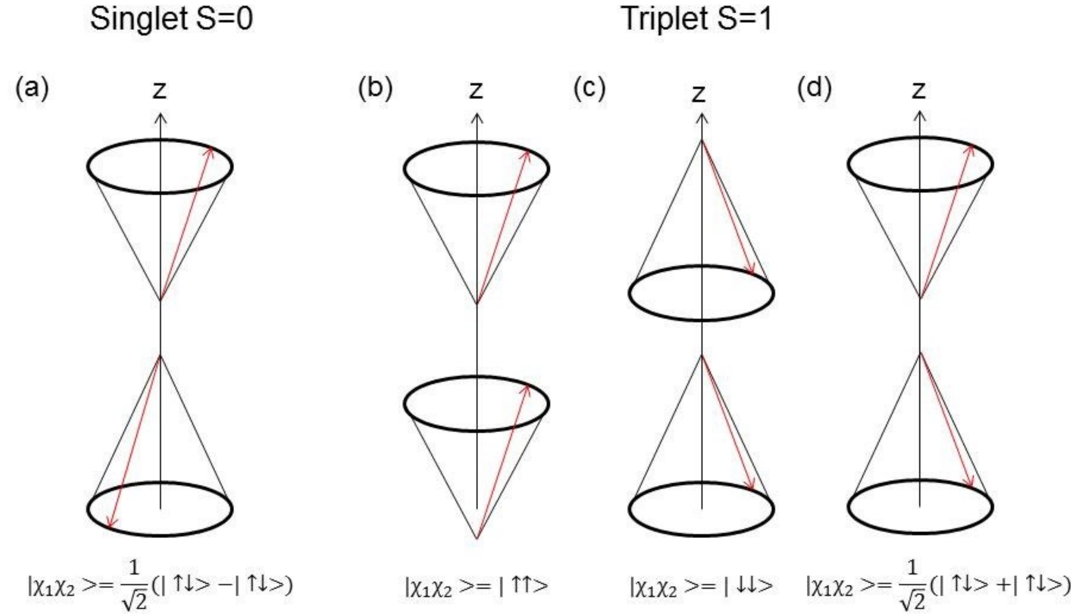

Figure 2.5 Illustration of four possible exciton spin combinations. **(a)** Singlet S=0; **(b)**, **(c)**, and **(d)** Triplet S=1. (Adapted from [99])

The PL efficiency (η_{PL}) is the ratio of emitted photons per absorbed photons for a given material. In our experiment, SiNCs typically have a η_{PL} >50% in solution. Detailed on the PL efficiency in SiNCs will be covered in Chapter 3 and Chapter 5 in this thesis.

2.4 Motivation of This Thesis

Following the discussion in previous section, with η_{OC}=0.2, γ=1, χ=0.25 and η_{PL}=1, the maximal theoretical EQE is calculated only to be 5%. However, it is noted that EQE

in our optimized SiNC-OLEDs is 8.6% (black curve in Figure 2.6). The calculation assumes the other 3 factors at maximum, so the increase in the device efficiency must come from an increase in the spin fraction χ. This gives the first motivation of the thesis, to explore the physical origin of high spin fraction in our SiNC-OLED, including measuring the accurate value for the spin fraction from experiment and determining possible mechanisms to explain it.

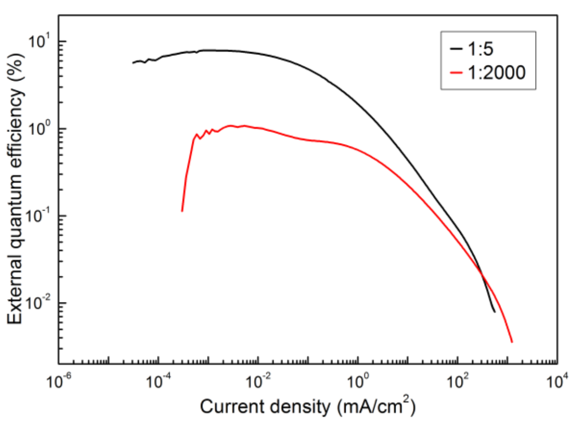

Figure 2.6 External quantum efficiencies of SiNC-OLEDs made from 1:5 (black) and 1:2000 (red) SiNCs. The ratio denotes the amount of ligand to solvent added during the functionalization step. (Data courtesy by Dr. Kai-Yuan Cheng)

As also can be seen from Figure 2.6, SiNCs passivated with different amount of ligands are used to fabricate device. Interestingly, it is found that less passivated 1:2000 sample (red curve in Figure 2.6) has a much lower efficiency, suggesting a possible difference in either electrical (γ) or optical properties (η_{PL}) due to change of passivation. This is another meaningful topic that calls upon our attention. Could we further improve the efficiency of the SiNC-OLED by engineering the surface ligands? To test these ideas, electrical and optical experiments on SiNCs will be conducted in the latter chapters.

To sum the goals of this thesis:

- Explore charge carrier transport (Chapter 4) and photophysics (Chapter 5) in SiNCs with different amounts of surface ligand passivation.
- Explore the physical origin of high spin fraction χ in SiNC-OLED. (Chapter 5 and 6)

Chapter 3 Experimental Procedures

3.1 Synthesis and Functionalization of Silicon Nanocrystals

3.1.1 Non-thermal Plasma Synthesis of Silicon Nanocrystals

Details on the non-thermal plasma synthesis of silicon nanocrystals (SiNCs) can be found in [100]. The SiNCs used in this thesis were supplied by Ting Chen in Prof. Uwe Kortshagen's research group at the University of Minnesota. Briefly, in order to prepare 5 nm SiNCs, silane in a mixture of He (5:95) and Ar at 12-14 and 25-30 sccm, respectively, are injected into a 9.5 mm o.d. Pyrex tube and are dissociated with 85-100 W of RF power at 1.4 Torr. The as-produced bare SiNCs formed in the plasma are then collected at the exhaust of the reactor on a stainless steel mesh, as shown in Figure 3.1(a). A transmission electron micrograph (TEM) of bare SiNCs is shown in Figure 3.2.

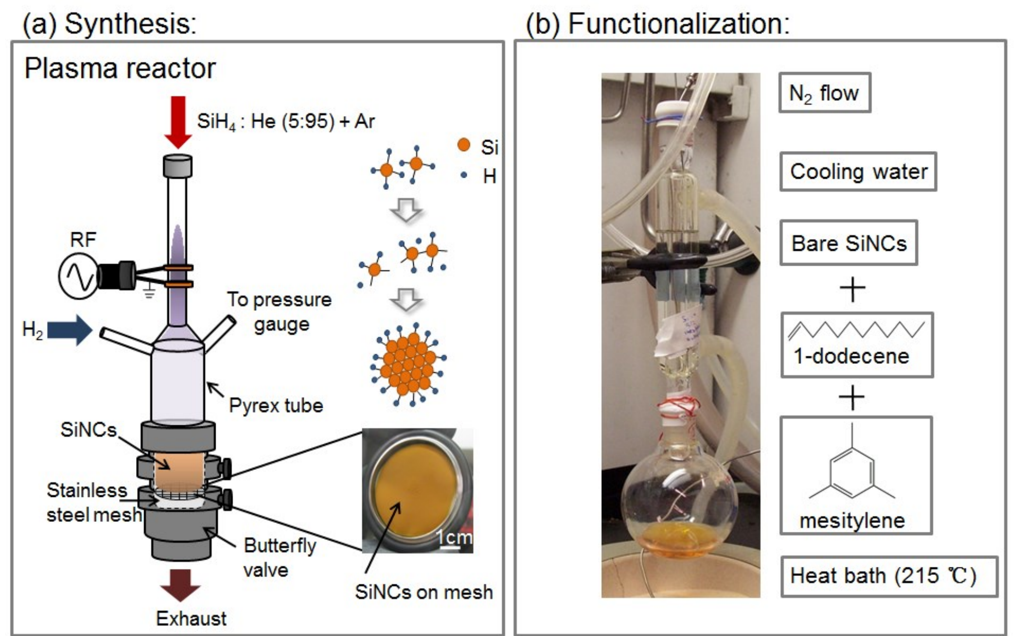

Figure 3.1 Pictures showing (a) non-thermal plasma synthesis and (b) functionalization of SiNCs. Photographs courtesy of Lorenzo Mangolini in Prof. Uwe Kortshagen's group.

The as-produced SiNCs, which are not passivated, only have a PL efficiency of ~10% in solution, which can be further enhanced [100]. One main reason for it is that the as-produced SiNCs are quickly oxidized when exposed to air. To prevent that, surface functionalization is thus required. More importantly, surface functionalization could also increase the solubility of SiNCs in non-polar solvents, which could be very useful in solution-based manufacture.

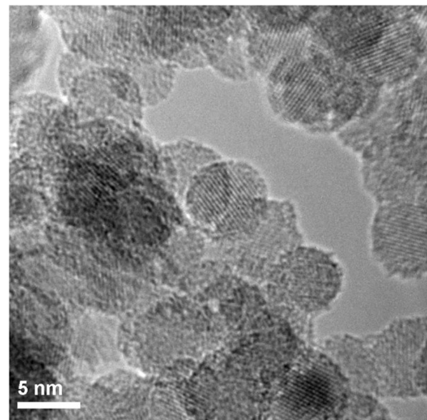

Figure 3.2 Transmission electron micrograph of silicon nanocrystals (SiNCs) synthesized in non-thermal plasma process. Picture courtesy by Lorenzo Mangolini in Prof. Kortshagen's group.

3.1.2 Functionalization of Silicon Nanocrystals

Surface passivation of the SiNCs is performed by dissolving the particles in a solution mixture of mesitylene and 1-dodecene and boiling at 205°C for 2-3 hours under reflux conditions, as shown in Figure 3.1 (b). After the functionalization step, the SiNCs are surface-terminated with Si-C covalent bonds [101], following the hydrosilylation reaction shown in Figure 3.3.

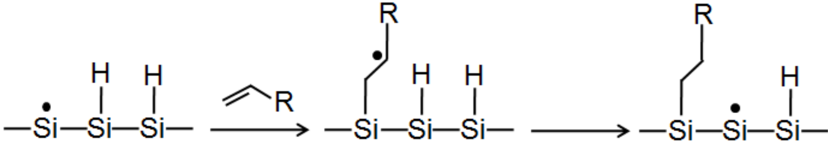

Figure 3.3 Proposed functionalization mechanism in SiNCs [101].

In our experiments, different amount of surface ligand coverage on SiNCs are achieved by changing the volume ratio of 1-dodecene over mesitylene in the

hydrosilylation solution. Here, we use 1:5, 1:1000 and 1:2000 to denote the volume ratio of these two. A rough estimation shows that for the 1:5 sample, ideally almost all the surface atoms on the SiNCs are passivated with ligands; while in 1:1000 sample, only half of the surface atoms are covered, as shown in Table 3.1.

Ratio of ligands v.s. solvent (mL/mL)	1:5	1:1000	1:2000
1-dodecene (mL)	6.7	0.04	0.02
Number of ligands	1.91×10^{22}	1.15×10^{20}	5.73×10^{19}
Ratio of ligands/particle	74609	449	224
Surface atoms/particle	909	909	909
Surface atom capping ratio	100%	49%	25%

Table 3.1 Surface SiNC atom capping ratio, calculated for adding 20 mg SiNCs into 40 mL hydrosilylation solution. Here it is assumed that all the ligands added can attach to the surface atom and each surface atom can only be in connection with a single ligand. Table courtesy by Ting Chen in Prof. Kortshagen's group.

3.2 Electrical Characterization

3.2.1 Current-Voltage Measurements

The devices used for current density-voltage (*J-V*) measurements are prepared following the scheme in Figure 1.6. Device substrates are first rinsed with Tergitol (from Sigma-Aldrich) and deionized water and sonicated for 5 min. Samples are then twice sonicated in acetone for 5 min. Finally, boiling isopropanol is used to clean residual organics off the substrate. The clean glass substrates are then dried with nitrogen gas and immediately put inside an Angstrom Engineering vacuum chamber for thermal evaporation of the bottom contact layer, either Al or Au. The SiNC solution (with a concentration of 20 mg/mL in chloroform) is then spun-coated on top of the bottom contact layer at different conditions. Finally, the device is thermally evaporated with top

metal contact again using a shadow mask, defining a device contact area of a circle in 1 mm diameter. All these steps are conducted in a nitrogen glove box.

Current density-voltage measurements are conducted in air ambient. A gold wire with a diameter of 25 μm is used to make top contact without damaging the device and a hard tungsten probe is used for bottom contact. The experimental data was collected by an Agilent semiconductor parameter analyzer 4155C. Device thickness is measured using tapping mode in a scanning probe microscopy (SPM). We scratch a trench on the SiNCs thin film using a razor blade and take the average height difference between the scratched and unscratched regions as the film thickness. Care must be taken to reduce the possible damage on the glass substrate by the blade. A typical thickness scan on SiNCs thin film is shown in Figure 3.4.

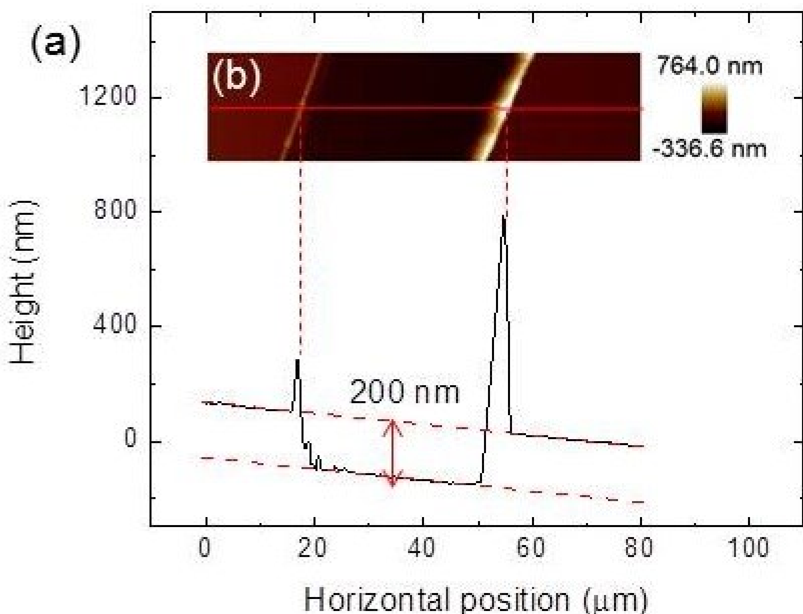

Figure 3.4 (a) Thickness versus horizontal position profile of the red solid line in the SPM image (inset **(b)**) of an Al/SiNC/Al device. The boundary of the trench is marked with red dashed lines. As the bottom contact Al electrode has a thickness of 100 nm, the real thickness of SiNC thin film is 100 nm.

3.2.2 Time-of-Flight Mobility Measurements

The device architecture used for time-of-flight (TOF) measurements is made on patterned ITO substrates. A schematic of the device is shown in Figure 3.5 (a), with a larger device area (3 mm by 3 mm). As in this experiment, the device is held vertically with large voltage bias applied, alligator clips are used to make electrical contact in replace of tungsten probes and gold wires.

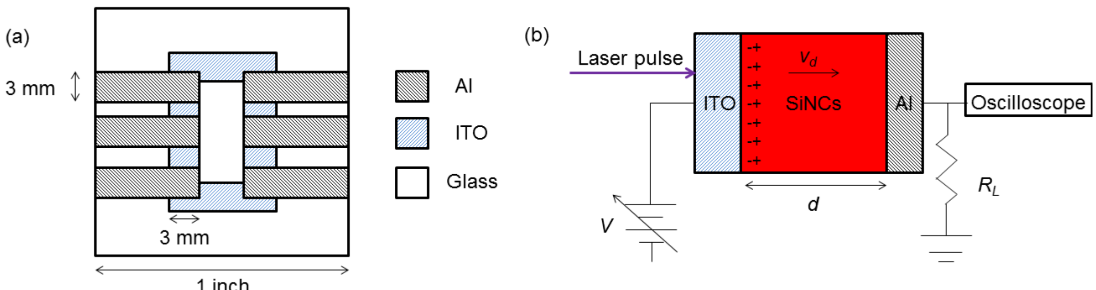

Figure 3.5 (a) Schematic patterned ITO substrate and **(b)** Experiment setup for mobility measurement of SiNCs using time-of-flight. *V* is the applied voltage on the SiNCs thin film and *d* is the film thickness. R_L is the load resistance and v_d is the speed of charge carrier.

In the experiment setup (Figure 3.5 (b)), a pulsed N_2 laser from Optical Building Blocks (337 nm in central wavelength and 800 ps in pulse width) pumps excitons in the SiNCs thin film and the generated excitons are quickly dissociated into charge carriers and then swept out by a strong applied electrical field (~10^6 V/cm). A Sorensen DC power supply (XHR600-1.7) is used as the voltage source and a Tektronix oscilloscope (TDS2004B) is used to measure the voltage change across the external load resistance to determine the amount of generated photocurrent. Neutral density filters and concentration lenses were used to focus the laser beam spot on the device under test at moderate illumination intensity. The hole mobility μ_h is measured by positively biasing ITO with respect to Al, and the reverse configuration can be used to probe electron mobility μ_e.

3.3 Optical Characterization

3.3.1 Room Temperature Steady-state Photoluminescence

In order to characterize SiNC PL, SiNCs were spun-cast onto clean glass or silicon (with native oxide) substrates, followed by baking on a hotplate at 64°C for 1 hour. Clean glass substrates are first put inside an integration sphere as a reference, under illumination at 385 nm (Hg lamp) (Figure 3.6 (a)). The SiNCs thin film sample is also put inside the same integration sphere to measure the change in the spectrum, as shown in Figure 3.6 (b). The spectral change around 385 nm is due to the absorption of SiNCs (black curve), while the change at infrared wavelength is due to their photoluminescence emission (red curve). The PL efficiency is obtained by dividing the integrated area of the emission curve over the area of absorption curve.

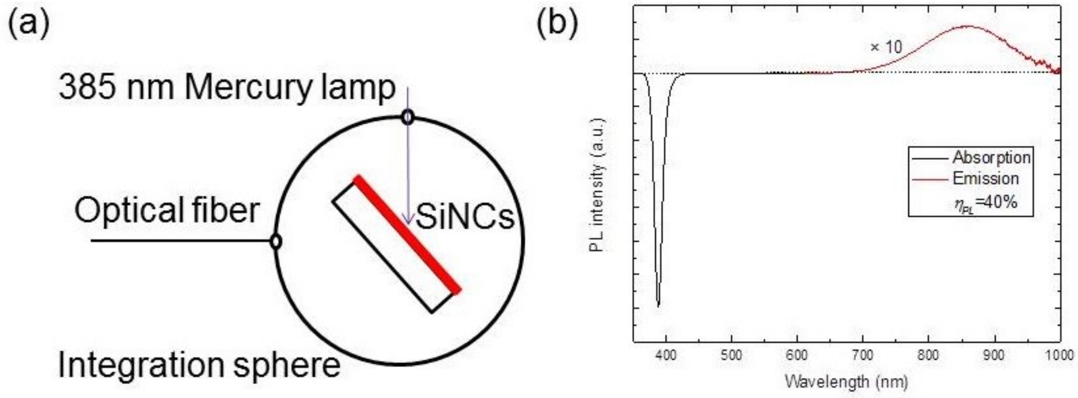

Figure 3.6 (a) Room temperature photoluminescence efficiency measurement setup. **(b)** Absorption and emission spectra of a 1:5 5 nm SiNC thin film sample.

A spectrometer (HR-USB2000) coupled to an optical fiber (from Ocean Optics, with a diameter of 1 mm) is used to capture the optical signal. In this experiment, an

integration time of 115 ms and an average of 50 times are applied.

3.3.2 Room Temperature Transient Photoluminescence

For measurements of transient PL, a small area photodectector with a diameter of 1 mm (PDA-10A from Thorlabs), coupled to an oscilloscope (Tektronix TDS2004B, with both 50 Ω and 1MΩ input) is used. The experiment setup is shown in Figure 3.7. A low-pass colored glass filter (450 nm, from Edmund Optics) is used to cut off the incident laser beam. An average of 100 scans is used in this experiment.

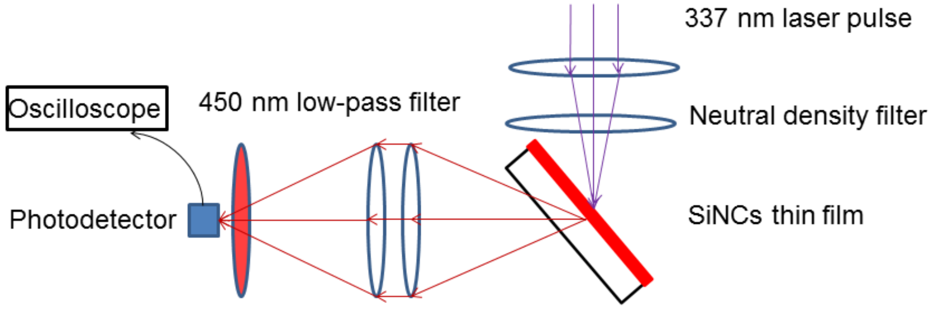

Figure 3.7 Room temperature transient photoluminescence testing setup.

3.3.3 Temperature Dependent Steady-state and Transient Photoluminescence

This experiment is conducted with a liquid nitrogen cryostat (VPF-100 from Janis) and the setup is shown in Figure 3.8. A Lakeshore 325 temperature controller with 2 thermal couples is used to change the temperature on the substrate from room temperature (296 K) to 78 K. A mechanical rough pump is also used to decrease the pressure inside the cryostat to 2.0 mTorr to reduce potential heat exchange to the room

ambient. Different from steady-state room temperature PL efficiency measurement, a 405 nm semiconductor laser with a power of 60 mW and spot size of 1 mm by 2 mm is used as the light source. In this case, the PL signal collection is limited by the geometry of the cryostat. So a longer integration time (1s) with 5 average times are used to increase the number of photons captured. The same setup is also used for capturing transient PL signal, but with PDA-10A photodetector in replace of using an optical fiber.

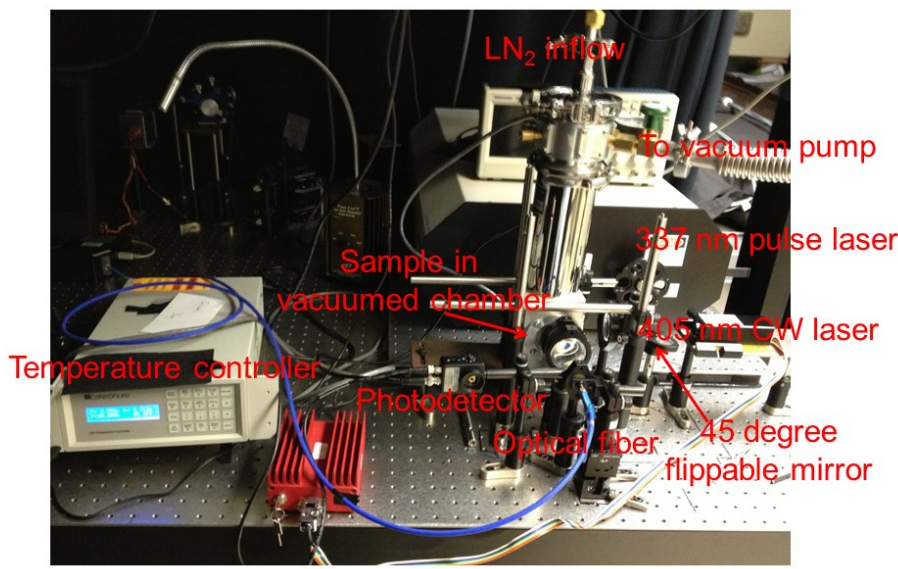

Figure 3.8 Temperature dependent photoluminescence measurement setup.

Chapter 4 Charge Transport in Silicon Nanocrystals

4.1 Foreword

As discussed in section 2.5, the external quantum efficiency of Si NC-OLEDs decreases significantly for less-passivated SiNCs. One possible reason is due to a decrease in the charge balance factor γ, or imbalance in charge carrier mobilities in SiNCs. So in this chapter, the electrical conductivity and mobility will be measured to explore the relationship between degree of passivation and charge transport in SiNCs.

Charge transport has been well studied in inorganic semiconductor nanocrystals [23, 59, 102-106]. However, most of the research is focused on characterizing the charge carrier mobilities using thin film transistors (TFTs) instead of simple J-V measurement [59]. In addition, chemical treatment [23, 102] and high temperature baking [103, 104] are frequently used on the NC films to reduce interparticle distance and help improve mobility. As we are interested in the intrinsic transport behavior of SiNCs in our SiNC-OLEDs, it is desirable to have them tested in a similar diode configuration without complicated treatment after the NC films are formed. Thus, following the energy band diagram in Figure 1.6, we construct devices (Figure 4.1 (b)) to probe the electrical properties in SiNCs.

4.2 Electrical Conductivity in Silicon Nanocrystals

We start with characterization of electron transport in SiNCs, using Al contacted device (Figure 4.1 (b)).

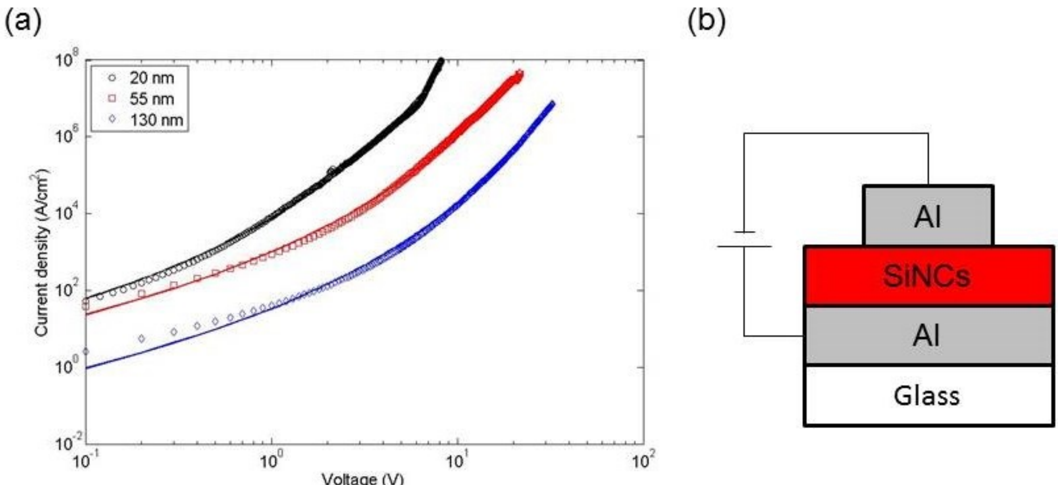

Figure 4.1 (a) Current density-voltage characteristics for 1:5 SiNCs as a function of film thickness (○:20 nm, □: 55 nm, ◇:130 nm) in a vertical device structure. Solid lines are fits. **(b)** Device structure for electron conductivity measurements. The device top contact has an area of a circle in 1 mm diameter.

The *J-V* plot can be fit well using Equation (1.24), Ohmic conduction with field-dependent mobility. It is expected that many traps are present in the NC thin film prepared by spin-coating. However, a clear transition point from higher order V^{l+1} (where l+1 is the slope of *J-V* curve in trap-limited SCLC and l>1) to V^2 dependence in *J-V* curve is not observed, thus the trap-free SCLC model (Equation (1.15)) cannot be applied here. One possible reason is that the current density is relatively high so that the device breaks down before it can reach the SCLC regime. This result differs from previous reports in which either trap-free [107] or trap-limited SCLC [108, 109] is observed in SiNCs. Such difference might come from both NC sizes and surface conditions. The extracted conductivity of the electron (σ_e) and Poole-Frenkel coefficient α are listed in Table 4.1.

Thickness (nm)	σ_e ($\Omega^{-1}cm^{-1}$)	α ($cm^{0.5}V^{-0.5}$)
20	3.66×10^{-8}	5.22×10^{-3}
55	6.42×10^{-8}	5.04×10^{-3}
130	6.73×10^{-9}	6.71×10^{-3}

Table 4.1 Electron conductivity and Poole-Frenkel coefficient for 1:5 SiNCs.

Here we are not able to determine the value for mobility μ_e because it is coupled with electron carrier density n_e. If the intrinsic carrier density in bulk Si n_i (10^{10} cm^{-3}) is taken as n_e, the calculated μ_e is on the order of 10^{-3} $cm^2V^{-1}s^{-1}$, a very high value for a NC device without any chemical treatment or high temperature treatment. It should be mentioned that in SiNCs where quantum confinement plays a role, both the energy band structure and the value of n_i change significantly. As a result, this estimation of μ_e may be inaccurate. In the 130 nm sample, the lower conductivity value suggests less close-packed film morphology and larger interparticle distance, which might result from a lower spinning rate (800 rpm).

The Poole-Frenkel coefficient α extracted from the fits is smaller than its theoretical value (α_{th}=8.57×10^{-3} $cm^{0.5}V^{-0.5}$) by using Equation (1.23) and ε_r=11.7 (bulk Si). The deviation in α can be explained using the model proposed by Hill [110]. In the original model [79] to derive α, the hole (atom core) is taken as immobile, which in fact it is not always true. Taking this modification into account, the effective Poole-Frenkel coefficient α_e is given by Equation (4.1), in which v_e and v_h are effective velocities of electrons and holes.

$$\alpha_e = \alpha\frac{2v_e - v_h}{2v_e} \approx \alpha\frac{2\mu_e - \mu_h}{2\mu_e} \tag{4.1}$$

Here we further assume the effective movement of electrons and holes are purely due to applied electrical field. So for bulk Si where $\mu_e >> \mu_h$, we will have $\alpha_e \approx \alpha$. If $\mu_e \approx \mu_h$, α will be reduced to half of its theoretical value, which has already been observed experimentally [111]. Using the fitted value of α in Table 4.1, we estimate that $\mu_e \approx 1.4\mu_h$. The balanced electron and hole mobility values suggest that electrons and holes have a high probability to form excitons right in the 1:5 SiNC emission layer, resulting in a high or nearly-unity charge balance factor γ.

Hole conductivity experiments are conducted using Au as contacts (Figure 1.6(b)), but turn out unsuccessful. The main reason is that Au, which is deposited at high temperature, may diffuse in the SiNC layer and induce unintentional doping or even short the device, especially for thinner NC films. Therefore we switch to time-of-flight (TOF) method to further explore the electrical properties in SiNCs.

4.3 Carrier Mobility in Silicon Nanocrystals

Few literatures [30, 112-114] have been reported before to evaluate the mobility of NCs using TOF technique. One reason is that it is often difficult to prepare a "thick" thin NC thin film and the as-prepared films have much larger RC delay time than typical organics, which could induce significant inaccuracy in the TOF measurement.

To check feasibility of TOF on our SiNCs, we first calculate the absorption length (λ) of SiNCs as ~10 nm, using an absorption coefficient of ~10^6 cm^{-1} at 337 nm pump wavelength [73]. Therefore, in a 300 nm thick thin film, it is reasonable to suppose that all the charge carriers are generated at or very close to the illuminated side (in our case,

ITO and SiNC interface). Further assuming that the carriers could drift to the opposite side under electrical field without any trapping, hopping or dispersion due to material inhomogeneity, mobility can thus be determined using Equation (4.2):

$$\mu = \frac{v}{F} = \frac{d/t_r}{V/d} = \frac{d^2}{Vt_r} \tag{4.2}$$

In which v is the velocity of charge carriers and t_r is the time of travel. The device thickness d can be measured with scanning probe microscopy as discussed earlier and transit time t_r can be read when the photocurrent (or photovoltage) vanishes. In more realistic cases, due to a spatial distribution of generated charge carriers, t_r is often taken as the midpoint of the decreasing transient photocurrent curve.

As in the case of NCs [30], charge transport in SiNCs is expected to be dispersive, where there is a significant distribution of inter-particle hopping times. Scher and Montroll [115] developed a detailed theoretical treatment to deal with such dispersive transients. They proposed that a considerable proportion of generated charge carriers will start to drift immediately after formation; while others will be immobilized to some long-range hopping sites (traps, for example) and will exhibit a longer transit time. As such, the transient photocurrent will be composed of one fast decay term and another slow decay term, which can be written as:

$$V(t) \propto \begin{cases} t^{-(1-\delta)}, & t \ll t_r \\ t^{-(1+\delta)}, & t \gg t_r \end{cases} \tag{4.3}$$

In (4.3), δ is a factor that characterizes the degree of dispersion or amorphism in the material, with 0 for purely crystalline and 1 for completely amorphous. In our SiNCs, δ typically has a value of 0.3±0.05, regardless of surface ligand coverage.

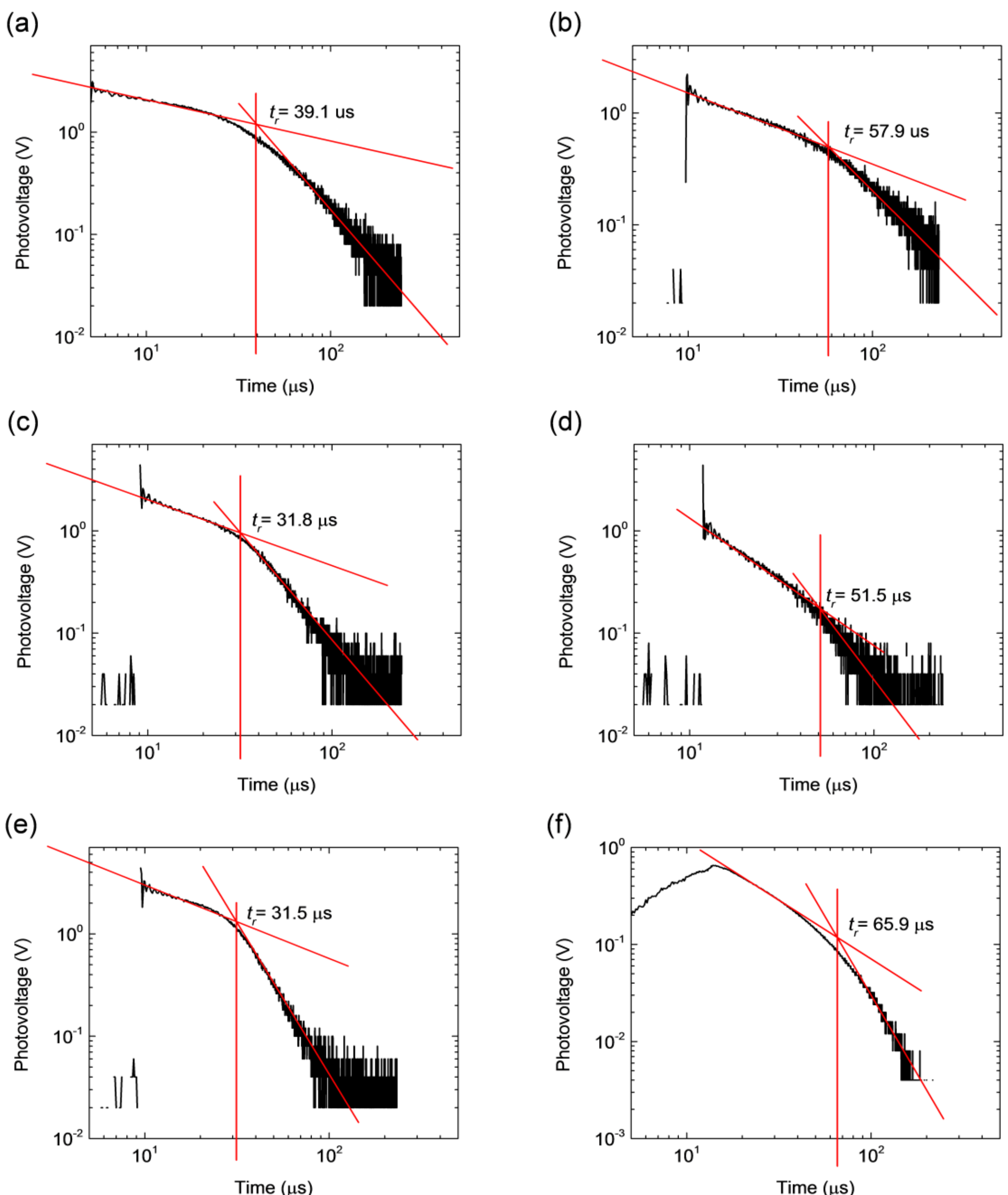

Figure 4.2 Time-of-flight mobility measurements of SiNCs: electron mobility in **(a)** 1:5 sample, **(c)** 1:1000 sample and **(e)** 1:2000 sample; and hole mobility in **(b)** 1:5 sample, **(d)** 1:1000 sample and **(f)** 1:2000 sample.

The transient photocurrent decay curve plotted in log-log scale can therefore be fitted with two straight lines and the intersection of these two lines is found to be the

transit time t_r. The physical meaning of t_r in fact is the time that "faster" charge carriers travel in the device.

The decay curves for 1:5, 1:1000 and 1:2000 SiNC samples are shown in Figure 4.2, and the extracted parameters are summarized in Table 4.2. All the data are obtained at 30 V.

SiNCs (*d*=300 nm)	1:5	1:1000	1:2000
t_r for electrons (μs)	39.1	31.8	31.5
t_r for holes (μs)	57.9	51.1	65.9
μ_e ($cm^2V^{-1}s^{-1}$)	7.87×10^{-7}	9.43×10^{-7}	9.52×10^{-7}
μ_h ($cm^2V^{-1}s^{-1}$)	5.32×10^{-7}	5.86×10^{-7}	4.56×10^{-7}
μ_e/μ_h	1.48	1.61	2.09

Table 4.2 Summary of 1:5, 1:1000 and 1:2000 SiNC electron and hole mobilities.

Interestingly, for 1:5 SiNC sample, it is found that $\mu_e \approx 1.48\mu_h$, very close to the derivation in section 4.2.1. This supports the use of an Ohmic conduction model with a Poole-Frenkel mobility to fit the *J-V* curve in Sec. 4.2. Also interesting is that, the mobility values for both electrons and holes in 1:1000 and 1:2000 samples are typically higher. This is not surprising since 1:1000 and 1:2000 samples are covered with fewer surface ligands.

It is also interesting to compare these mobility values with our previous study [34], in which different electron transport materials with different thicknesses are utilized to fabricate SiNC-OLEDs. It is found that the device EQE changes only a little when using high electron mobility chemicals, such as N,N'-dicarbazolyl-4-4'-biphenyl (CBP, $\mu_e\sim 5\times10^{-4}$ $cm^2V^{-1}s^{-1}$ at 0.5 MV/cm [116]). However, EQE suffers significantly when 40 nm low electron mobility material 4,4',4''-tris-(N-carbazolyl)-triphenlyamine (TCTA,

μ_e~10^{-8} $cm^2V^{-1}s^{-1}$ [117]) is used. This suggests that charge transport in our SiNC-OLEDs is limited by the low mobility (on the order of 10^{-7} $cm^2V^{-1}s^{-1}$) of SiNCs. A wide range of higher mobility organic semiconductors become possible candidates for fabricating SiNC-OLEDs as long as their energy levels could confine excitons in the SiNC emission layer (Figure 2.3).

If we take the electron mobility value and conductivity extracted from *J-V* measurements using Equation (1.12), the carrier density is 5×10^{16} cm^{-3}, 6 orders of magnitude higher than intrinsic carrier density n_i in bulk Si. To explain this huge difference, the field dependent mobility also needs to be taken into consideration. If we further apply the Poole-Frenkel coefficient α from Table 4.1, the corrected carrier density is 6×10^{13} cm^{-3}, which is smaller than the value (4~9×10^{14} cm^{-3}) reported in [107], in which SiNCs are capped with SiO_2 shell. The difference is likely due to change in surface conditions.

Mobility measurement at different electrical field is unsuccessful. At lower field, the plot only reveals a single linear decay (instead of two) in log-log scale, which might result from the fact that not all the generated excitons are effectively dissociated. While at higher field, the device easily breaks down.

As pointed at the beginning of this section, to strictly evaluate the transit time t_r, the RC delay of the time-of-flight testing circuit is also calculated. Taking the device as a planar capacitor, the capacitance can be determined using Equation 4.4. Here we take bulk Si dielectric constant (ε_r=11.7) and use device area $A=9\times10^{-6}$ m^2 and thickness d=300 nm, C is calculated as about 3 nF.

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \tag{4.4}$$

The resistance used the experiment is 1000 Ω. Thus the RC delay time constant is about 3 μs, which is an order of magnitude smaller than t_r. To further decrease the RC delay time and make more accurate measurements on mobility, a 50 Ω resistor is also tried. However in this situation, the initial faster decay is too small to be detected.

4.4 Summary

In this Chapter, electrical properties of SiNCs with different degrees of surface ligands passivation are measured with current-voltage (J-V) and time-of-flight (TOF) measurements. It has been found that 1:5 SiNCs are characterized by Ohmic conduction with zero-field electron conductivity on the order of 10^{-8} Ω^{-1}cm, and Poole-Frenkel coefficient ~5×10^{-3} $cm^{0.5}V^{-0.5}$. Both electron and hole mobilities are obtained with TOF technique, with their values are on the order of 10^{-7} $cm^2V^{-1}s^{-1}$. With less surface ligand coverage, the difference between electron and hole mobility increases, which could help explain the decrease in γ and EQE in our SiNC-OLEDs.

Chapter 5 Silicon Nanocrystal Photoluminescence

5.1 Foreword

In the previous chapter, the electron and hole mobilities of SiNCs passivated with differing degrees of surface ligands coverage were characterized. The mobility imbalance could be a possible reason for the decrease in efficiency at high current density observed SiNCs. However, it is also possible that ligand coverage could also induce changes in the PL efficiency (η_{PL}).

In the research of PL from SiNCs, two questions remains in debate. One is the origin of PL in SiNCs. Some of the literature argues that the PL in SiNCs originates from core states, due to strong quantum confinement. Their proof mainly comes from characteristic-phonon-assisted PL [81], size dependent emission energy [68, 118], and sensitivity of PL spectra to large pressure [119]. While other reports argue that the emission is related to the surface defects in the SiNCs. Experimental support arises from sensitivity to chemical treatments [120], insensitivity to large magnetic fields [121], and long-lived PL decay (on the order of μs) [122]. There is also work arguing that both surface and core states contribute to PL [17].

Another interesting topic is the decay mechanism and formula for transient PL. Most researchers [10, 123-128] are inclined to use stretched exponential (Equation (1.29)). To explain the deviation from ideal single exponential decay, Auger process [124] and exciton transfer process [128] are often considered. However, no solid experimental proof has been offered. Other mechanisms are also proposed. For example, a two-level system [129] has been considered due to possible a singlet-triplet transition at low

temperature; multi-exponential decay fit [83] has been used due to size distribution in SiNCs; bi-exponential is utilized to explain two different types of emission states (surface and core) [17]; and single exponential is used by people who believe core-only or surface-only emission [68, 130].

In this chapter, we will explore these questions and offer insight into the underlying mechanisms of PL in SiNCs through series of surface ligand coverage dependent, temperature dependent and size dependent PL experiments.

5.2 Room Temperature Photoluminescence

To examine whether ligand coverage plays an important role in SiNC PL, the thin film PL was measured at room temperature, as described in Chapter 3. Due to rapid oxidation (especially under UV light exposure) in samples with fewer ligands, PL is measured immediately after removing the samples from a N_2 glovebox. The steady-state and transient PL behaviour are plotted in Figure 5.1 (a) and (b) respectively.

Interestingly, it is found that changes in surface ligand coverage do not play a significant role in impacting emission wavelength, intensity and exciton lifetime, as listed in Table 5.1. In other words, surface modification does not significantly change the PL in SiNCs, which suggests that the origin of PL is core emission.

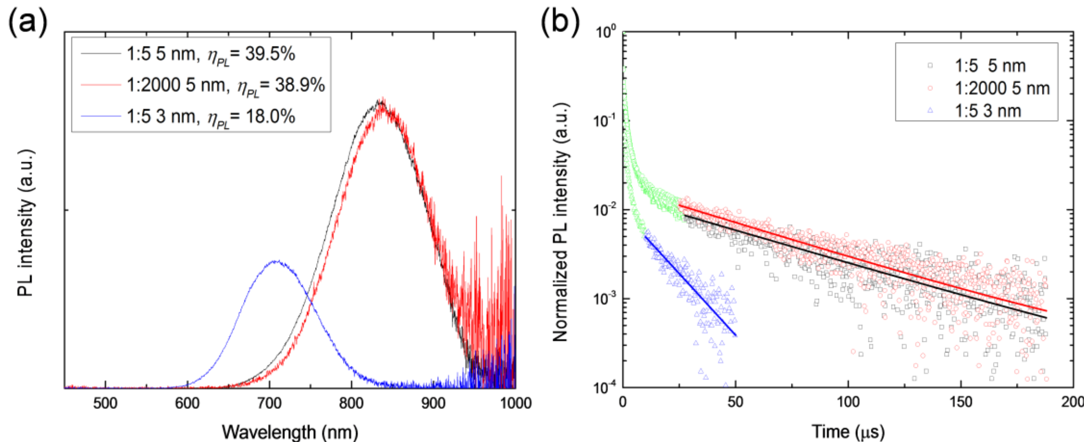

Figure 5.1 (a) Steady-state photoluminescence spectra and **(b)** transient photoluminescence decay of 1:5 5 nm (□), 1:2000 5 nm (○) and 1:5 3 nm (△) SiNCs thin film. The masked data points are in green and the rest points are fitted with a single exponential decay (straight line in the plot).

Size (nm)	5	5	3
Ligand ratio	1:5	1:2000	1:5
Peak wavelength (nm)	834	839	711
η_{PL}	39.5%	38.9%	18.0%
τ (μs)	59.7	58.8	16.6
k_r (×10^3 s^{-1})	6.62	6.62	10.84
k_{nr} (×10^3 s^{-1})	10.1	10.4	49.4

Table 5.1 Summary of steady-state and transient photoluminescence measurements on SiNCs with varying size and ligand coverage ratio at room temperature (296 K).

For the transient PL decay, the stretched exponential fails to provide a good fit. Here we select the region where the curvature ends (typically under ~1% of normalized peak intensity in this testing configuration) and fit with a single exponential. A similar method has been used before in both CdSe NCs [60] and SiNCs [68]. The authors of these papers attribute the faster decay at short times to either the laser pulse or RC delay of the detection circuit. In our measurement, the lifetime of faster decay is ~1 μs, which is much

slower than the pulse width of the laser (800 ps). We also tried to measure steady-state spectrum using pulsed laser (Figure 5.2). Due to extremely small duty cycle (~ 10^{-8}), the signal to noise ratio is low. However, no emission peak other than SiNCs is observed, proving that neither laser nor colored glass filter emission play a role in the transient PL decay.

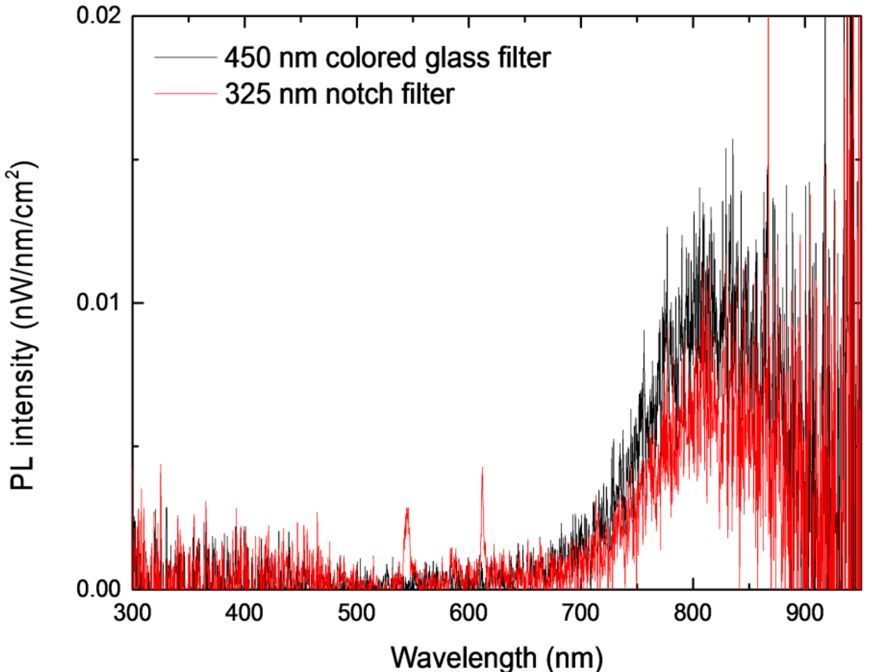

Figure 5.2 Photoluminescence emission spectra of SiNCs excited by a pulsed laser (duty cycle ~10^{-8}). The colored glass is a low-pass filter which cuts off the emission over 450 nm in wavelength. The notch filter is OD 4 and has a reflectivity >99.99% around its central peak wavelength (325 nm).

For the 1:5 5 nm SiNCs thin film sample, transient PL is collected as a function of illumination intensity, as shown in Figure 5.3. The extracted lifetimes are similar: at 34 mJ/cm^2, τ=59.7 μs; at 16 mJ/cm^2, τ=58.8 μs; and at 5.5 mJ/cm^2, τ=60.4 μs. For the sample with highest intensity, the calculated number of photons in the illuminated region (6.6 mm×3 mm×160 nm) is ~1.2×10^{15}, which is 3 orders of magnitude higher than the

number of SiNCs (~ 6.7×10^{12}). No additional exciton decay routes open even with such high exciton concentration. This suggests that Auger process is unlikely to occur in our SiNCs over these ranges.

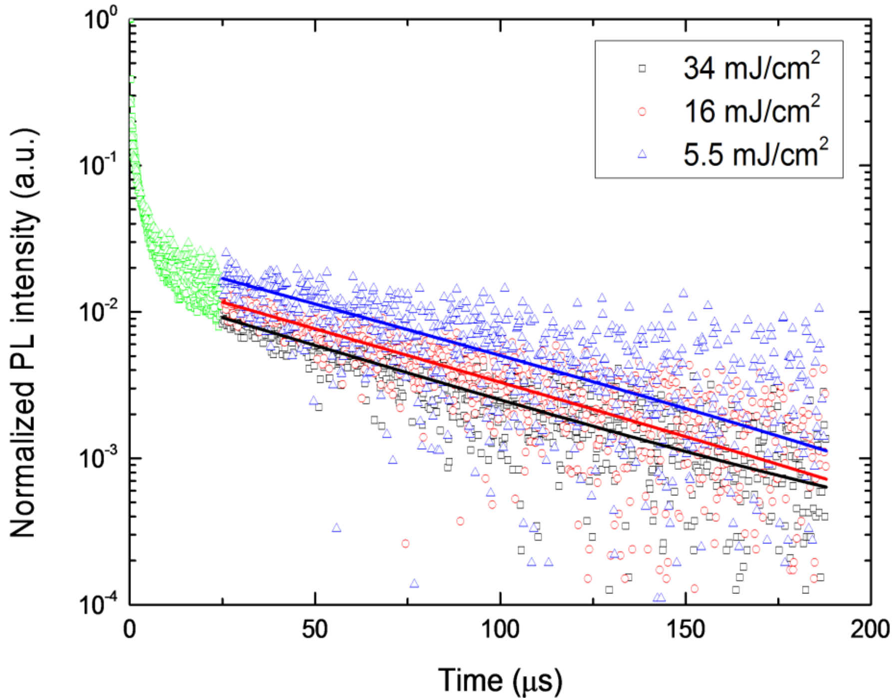

Figure 5.3 Transient photoluminescence decay of 1:5 5 nm SiNCs at different pump intensities, □: 34 mJ/cm^2, ○: 16mJ/cm^2 and △: 5.5 mJ/cm^2. The masked data points are in green, and are not included in the fit (straight lines in the plot).

Using the values of η_{PL} and τ, we also could calculate both radiative (k_r) and non-radiative (k_{nr}) decay rates using Equation (1.25). For smaller SiNCs, k_r is higher, which can be explained by the increase in spatially overlapped wavefunction [2]. However, it still remains unclear why k_{nr} varies with NC size. To study the origin of this observation, we conduct temperature dependent measurements. As 1:5 and 1:2000 samples show almost identical optical properties, only 1:5 (5 nm and 3 nm) samples are tested later.

5.3 Temperature Dependent Photoluminescence

5.3.1 Steady-state Photoluminescence

Figure 5.4 shows steady-state PL collected as a function of temperature. It is found that as the temperature decreases, integrated PL intensity and energy bandgap both increase. Here, we simply take $\frac{hc}{\lambda_{peak}}$ as the bandgap energy, similar as in [127].

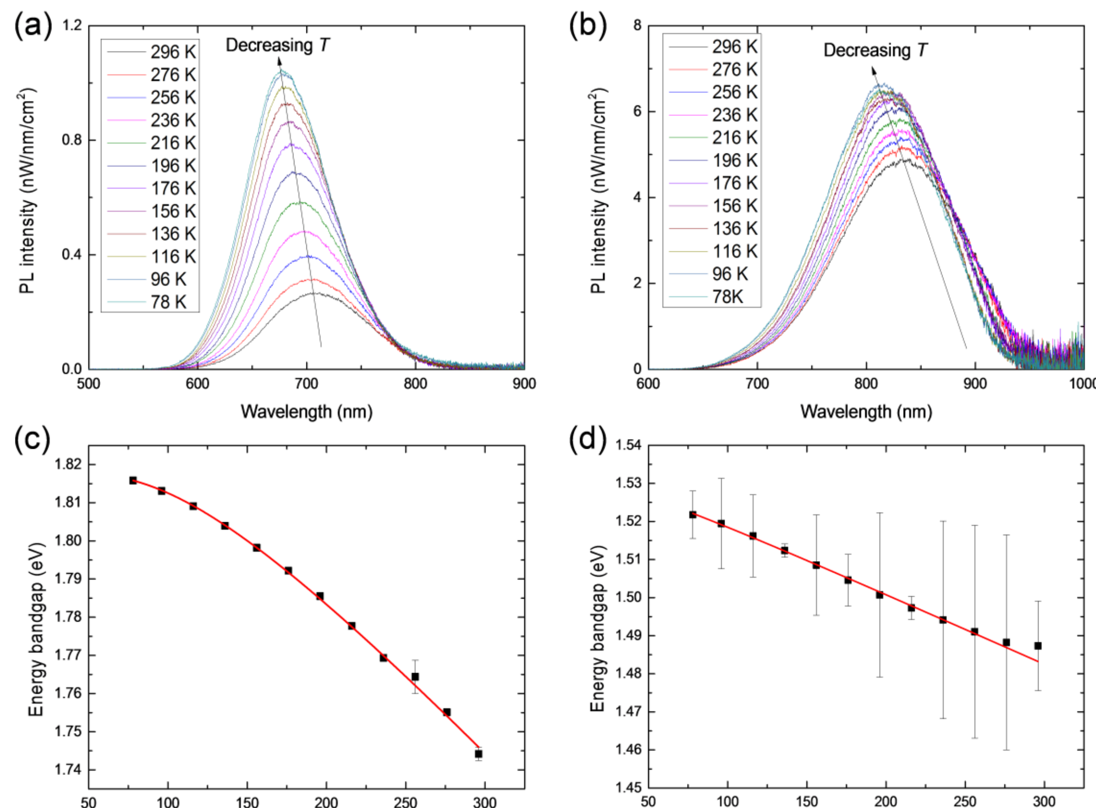

Figure 5.4 Steady-state photoluminescence spectra for **(a)** 3 nm and **(b)** 5 nm SiNCs at different temperatures, and energy bandgap of **(c)** 3 nm and **(d)** 5 nm SiNCs at different temperatures.

The temperature dependence of the energy bandgap in bulk semiconductors is usually explained by Varshni's formula [131], which states that:

$$E_g(T) = E_g(0) + \frac{AT^2}{T+B} \tag{5.1}$$

In this equation, $E_g(0)$ is the bandgap at 0 K, A and B are material constants. In [131], Varshni relates B to Debye's temperature. However, this assumption carries no physical background and fails to explain bulk Si (fitted value 1108 K, compared with theoretical value 645 K). Significant offset in fitting with this equation is also observed in SiNCs [127].

It is known that thermal contraction induced size change on NCs could induce additional confinement [2]. However, using the thermal expansion coefficient of bulk Si [132], the calculated reduction in NC size is small ($<10^{-4}$), so this possibility is ruled out.

In order to explain the temperature dependence, we follow the model in [133], in which the bandgap E_g is described as:

$$E_g(T) = E_g(0) - S\frac{<\hbar\omega>}{exp\left(\frac{<\hbar\omega>}{k_B T}\right)-1} \tag{5.2}$$

where S is the electron-phonon coupling coefficient, $<\hbar\omega>$ is the average phonon energy, and the expression, $\frac{1}{exp\left(\frac{<\hbar\omega>}{k_B T}\right)-1}$ is Planck's distribution function of phonons. This model assumes that electrons in the valence band could cross the bandgap with the aid of ambient phonons. As the temperature decreases, there are fewer phonons at the average energy to participate in this process, making the transition more difficult. The fitted values are listed in Table 5.2.

NC size	$E_g(0)$	$<\hbar\omega>$	S
3 nm	1.82 eV	29.7 meV	5.31
5 nm	1.53 eV	9.0 meV	2.15

Table 5.2 Zero temperature bandgap, average phonon energy and coupling coefficient of 3 nm (Figure 5.4 (c)) and 5 nm SiNCs (Figure 5.4 (d)) using Equation (5.2).

In 3 nm SiNCs, the average phonon energy <$\hbar\omega$> is 29.7 meV, which is close to the reported value of bulk Si (25.5 meV) [133]. The small difference could be due to additional momentum conservation phonons in NC system. However, the fitted value for 5 nm sample is only 9 meV, which deviates greatly from bulk value. One possible reason is that the energy bandgap in close packed NC solid is not dominated by individual NCs, but a collective behavior [19]. In larger SiNCs (5 nm) where the inter-particle separation is longer, potential overlap of wavefunctions between adjacent NCs is reduced. In smaller NCs (3 nm), on the other hand, exciton wavefunctions overlap much more, and could be continuous even including interparticle barriers, which is comparable to bulk materials where wavefunction is continuous everywhere.

It is also interesting to study the change in PL intensity and shape as a function of temperature. The spectrum appears as a single Gaussian peak between 78 K to 296 K, which supports our idea that the only one emission state exists in the SiNCs. Further, as surface modification changes only a little in η_{PL}, it is concluded that this emission must be from core states.

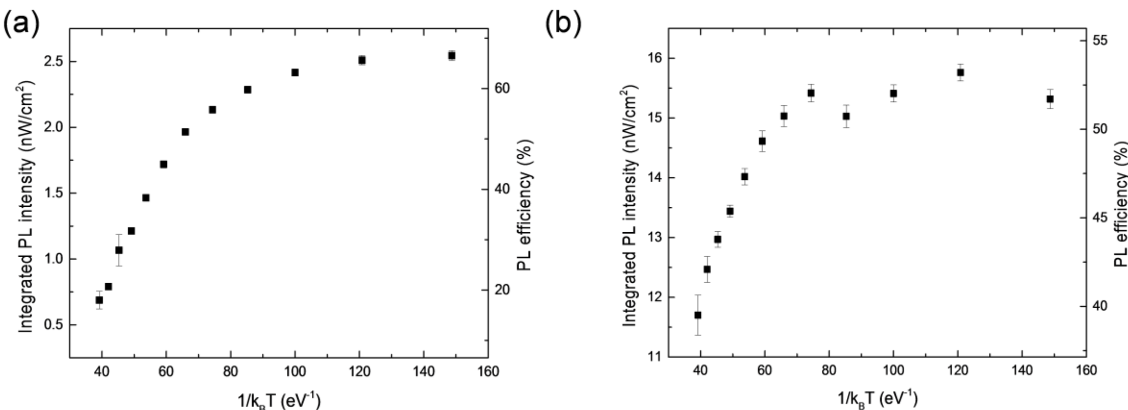

Figure 5.5 PL efficiency (η_{PL}) derived from integrated PL intensity versus temperature of **(a)** 3 nm and **(b)** 5 nm SiNCs.

In Figure 5.5, we plot η_{PL} versus temperature by integrating the area under the spectra, assuming that absorption does not strongly changes over the studied temperature range. In order to further extract the values of k_r and k_{nr}, temperature dependent lifetime study is also conducted.

5.3.2 Transient Photoluminescence

The PL transient decay of 1:5 5 nm and 3 nm SiNCs at different temperatures are shown in Figure 5.6. At room ambient measurement, the top region (~90% intensity) is not included in the fitting. As the testing is performed in an optical cryostat which limits the collection of PL emission, signal to noise ratio is typically lower. It is also noticed that the proportion of top region changes from ~ 99% to ~ 90%, but the fitted lifetime at room temperatures are similar (see Figure 5.7). This invalidates the assumption that two different types of emission states are involved in SiNC PL, as the real transient decay rate does not depend on collection geometry.

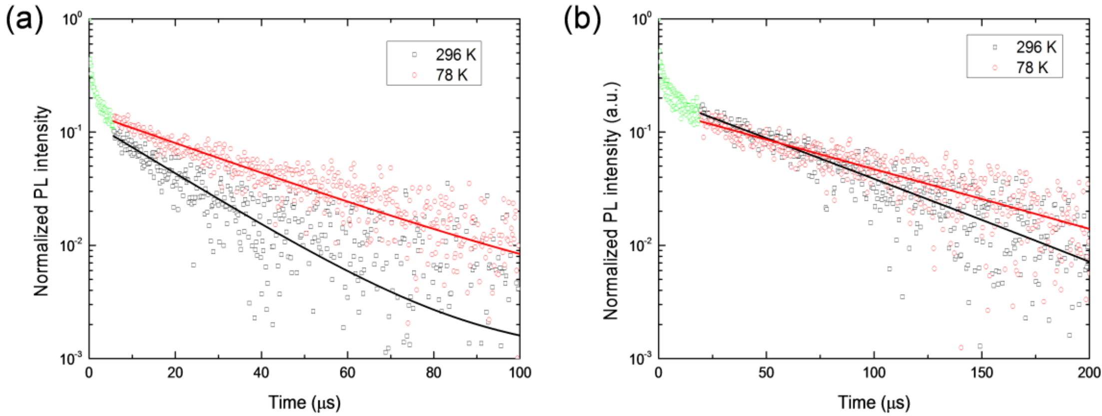

Figure 5.6 Transient photoluminescence decay curve at 296 K (□) and 78 K (○), **(a)** 1:5 3 nm SiNCs and **(b)** 1:5 5 nm SiNCs. The masked data points are in green.

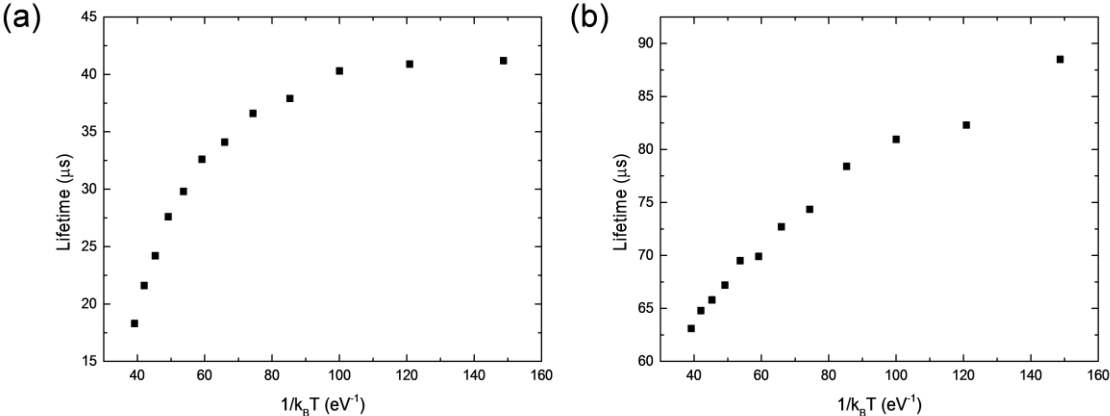

Figure 5.7 Fitted lifetime values of **(a)** 3 nm SiNCs and **(b)** 5 nm SiNCs at different temperatures.

Using Equation (1.25), Figure 5.5 and 5.7, radiative and non-radiative exciton decay rates (k_r and k_{nr}) at different temperatures are calculated, as shown in Figure 5.8. k_r in 3 nm SiNCs is higher than in 5 nm, which is likely due to the increase in wavefunction overlap [2]. However, different from the assumption in some literatures [61, 63, 127], k_r is found not to be a constant with temperature. In CdSe NCs [60], it is argued that two types of radiative decay exists: direct recombination and phonon-assisted recombination, which is temperature dependent. This argument might be helpful to explain the change of k_r with temperature in SiNCs.

For the non-radiative decay rate (k_{nr}), we find it to be thermally activated, which follows Arrhenius's law with an additional constant term k_0 taken into account:

$$k_{nr}(T) = k_a \, exp\left(-\frac{E_a}{k_B T}\right) + k_0 \tag{5.3}$$

Fitting results are listed in Table 5.3. It is found that at low temperature where the non-radiative process is effectively quenched, η_{PL} still deviates greatly from unity. This can be explained by the constant term k_0 in Equation (5.3), which is probably from the indirect

bandgap nature in Si. Similar argument [68] has been made previously which states that SiNCs are still indirect or quasi-direct bandgap materials even with momentum break-down due to uncertainty principle.

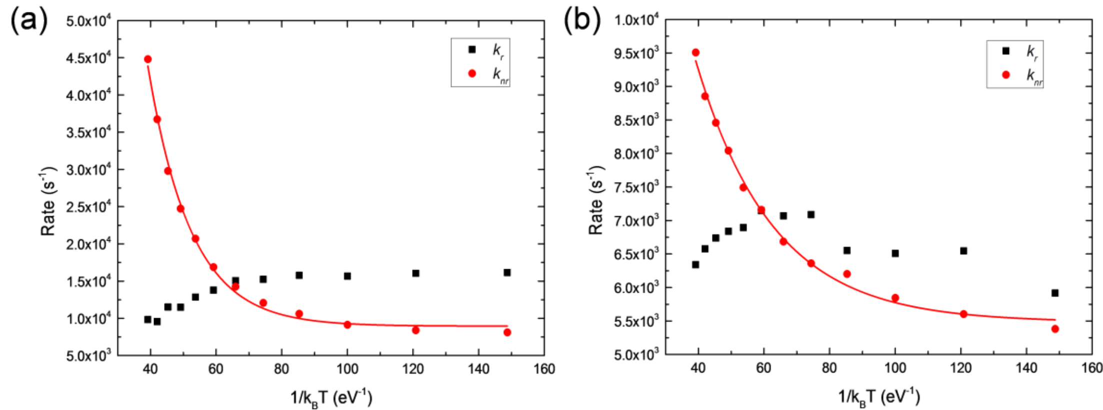

Figure 5.8 Calculated radiative (k_r) and non-radiative exciton decay rate (k_{nr}) at different temperatures of **(a)** 3 nm SiNCs and **(b)** 5 nm SiNCs.

NC size	k_a	E_a	k_0
3 nm	6.94×10^5 s^{-1}	76.3 meV	8.95×10^3 s^{-1}
5 nm	2.07×10^4 s^{-1}	42.6 meV	5.48×10^3 s^{-1}

Table 5.3 Decay rates and activation energy of 3 nm (Figure 5.8 (a)) and 5 nm SiNCs (Figure 5.8 (b)) using Equation (5.3).

E_a is the activation energy of non-radiative decay and is greater in smaller SiNCs, which could be related to the exciton binding energy in SiNCs [4]. As the size of NC decreases, dielectric constant will go down, which will increase the exciton binding energy according to Bohr's model [64]. We notice that our experimental value is smaller than the calculated value (82 meV for 3 nm SiNCs) in literature [134]. This is probably because in the calculation, dielectric constant is taken as a constant with temperature, while in our case, temperature may play a significant role.

5.4 Summary

In this Chapter, PL of SiNCs thin film samples with different degrees of surface ligand passivation and with different sizes are characterized by steady-state and transient measurements at different temperatures. It has been found that surface modification does not strongly affect η_{PL} in SiNCs. Further, through the single exponential fitting of transient PL, it is concluded that the origin of PL in SiNCs is only due to core emission states. We also noticed that electron-phonon coupling is likely responsible for the energy bandgap broadening in SiNCs as temperature decreases. In addition, k_{nr} of SiNCs is explained with an Arrhenius equation, in which the activation energy is probably the exciton binding energy and the constant term is due to the indirect bandgap nature in SiNCs.

Chapter 6 Conclusion and Future Research Proposal

6.1 Conclusion

The main goal of this thesis is to investigate device physics and study the origin of high efficiency in Si NC-OLEDs. This was done by thoroughly characterizing the electrical and optical properties in SiNCs. A deeper understanding of these properties in SiNCs might be beneficial for designing highly efficient Si NC-OLEDs and other NC-OLEDs as well. This chapter will sum up the results achieved so far and propose future directions for research.

In Chapter 4, the electrical conductivity and mobility in SiNCs with different degrees of surface ligand coverage were measured. It was found that electron transport in SiNCs is defined by Ohmic conduction with an electrical field-dependent mobility. Electron and hole mobilities, determined with the help of time-of-flight (TOF) measurements, are both on the order of 10^{-7} $cm^2V^{-1}s^{-1}$. This suggests that the transport in Si NC-OLEDs is limited by the SiNC layer and further supports the exciton confinement model proposed previously. In addition, as the degree of ligand coverage decrease, an increased mobility imbalance is observed which might explain the drop in external quantum efficiency.

In Chapter 5, a complete photoluminescence (PL) study was performed. Ligand coverage dependent studies at room temperature reveal that surface modification does not strongly impact the PL in SiNCs. Pump power dependent studies shows that Auger exciton recombination process is unlikely. Size dependent studies show that smaller SiNCs tend to have a larger exciton decay rate.

More interestingly, temperature dependent PL experiment supports the thought that the emission in SiNCs is due only to core states. Both the energy bandgap and PL intensity of SiNCs increase as the temperature is reduced. The former is explained through electron-phonon coupling model. The latter is due to the reduction of non-radiative decay rate (k_{nr}), which is characterized by Arrhenius law. The activation energy (E_a) of k_{nr} is likely from exciton dissociation.

6.2 Charge Mobility using Lateral Patterned Devices

In Chapter 4, the vertical device structure (Figure 4.1(b)) was tried to extract mobilities from current-voltage measurement. However, limited by the spin-coating technique, device thickness is typically smaller than 300 nm so that device tends to break down due to high current density before entering SCLC regime. For the same reason, hole measurement is unsuccessful due to the high diffusivity of Au atoms (top metal contact) at high temperature. More importantly, uniformity in thickness is always a problem. Thickness difference exists between center and corner, especially at low spinning rate.

In order to solve these problems, an interdigitated lateral device architecture will be used, as show in Figure 6.1. The device has 100 sets of electrodes (channels) in total and the spacing (channel width L) between each two adjacent electrodes is fixed at 5 μm, which on average could give a more accurate result than a single vertical device. The SiNCs are spun-coated into the channel without further high temperature treatment. The metal electrodes will be either Al or Au, which allows electron-only or hole-only

transport, as discussed earlier. The electrodes are deposited before spin-coating process so that metal diffusion will not become a problem.

To further clarify the transport mechanism, the interdigitated lateral device will first be tested in standard two probe *J-V* measurement. Due to a larger device thickness, a high voltage source (up to 200 V) will be used for the testing.

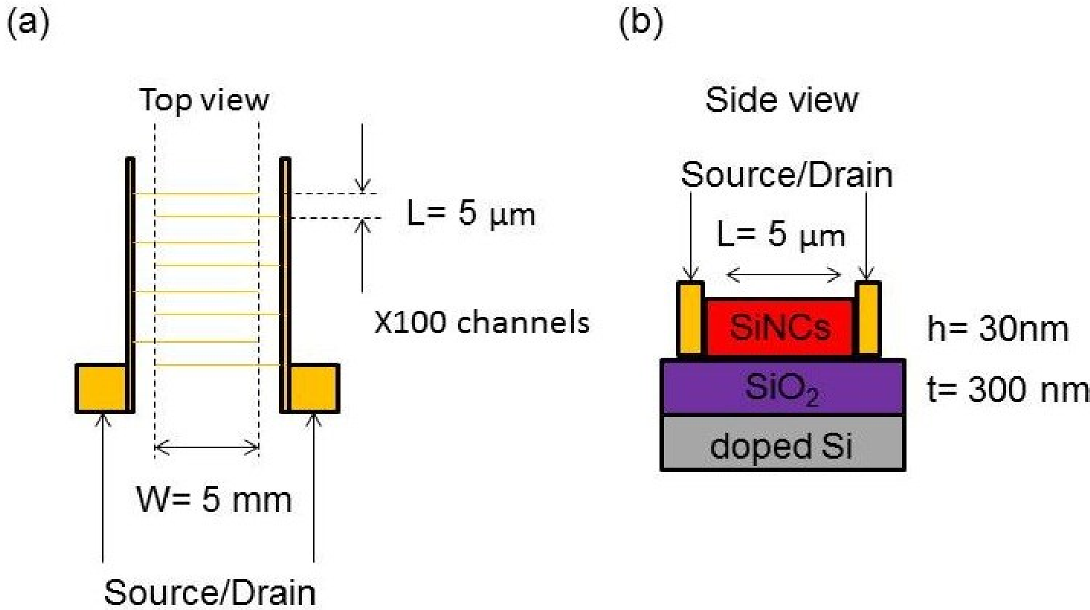

Figure 6.1 Top view **(a)** and **(b)** side view of the interdigitated lateral device.

The advantage of this device is it can also be tested as a FET. At low drain voltage (V_d), drain current (I_d) increases linearly with V_d, the mobility in this regime (μ_{lin}) can be calculated from the slope of I_d vs. V_g plot, as shown in Equation (6.1). V_g is the gate voltage, L is channel length, W is channel width and C' is the capacitance of silica layer per unit area, which can be calculated using Equation (6.2). At high V_d ($V_d >> V_g - V_T$, where V_T is the threshold voltage), mobility tend to saturate and can be calculated using Equation (6.3).

$$\mu_{lin} = \frac{\partial I_d}{\partial V_g}\frac{L}{CV_dW} \quad (6.1)$$

$$C' = \frac{\epsilon_{SiO_2}}{t} \quad (6.2)$$

$$\mu_{sat} = \left(\frac{\partial\sqrt{I_d}}{\partial V_g}\right)^2\frac{2L}{C'W} \quad (6.3)$$

The mobility at zero electrical field in Ohmic conduction regime μ_0 can be approximately taken as μ_{lin}, so from Equation (1.12), carrier density n can also be extracted. The obtained values of n and μ_{sat} could also be compared with the results from TOF measurements. This experiment could serve as an additional proof for the mobility of SiNCs.

6.3 Spin Fraction in Hybrid SiNC-OLEDs

6.3.1 Exciton Spin Fraction Measurement

As discussed earlier, typically allowed emitting fraction for exciton states in organic emitter is 25% for the fluorescent OLEDs and 100% for phosphorescent OLEDs. The increase of spin fraction in phosphorescent materials is mainly due to strong spin-orbit interaction, where triplet states (75% of the total excitons) could be allowed for radiative recombination [91]. In phosphorescent OLEDs, usually an organometallic chemical that contains a heavy metal atom, such as Iridium (Ir), is involved. The heavy element, which has a high orbital momentum, could help overcome the momentum conservation and facilitate triplet recombination. While exciton spin fraction has been well studied in organic semiconductors [91, 135-137], to our best knowledge, very few researches have been conducted to define and confirm spin statistics of the exciton states in highly

luminescent SiNCs.

Silicon, as a light atom, is usually considered not able to support enough orbital momentum, nor giving phosphorescence. But it should be mentioned that it is still possible for over 25% of the total exciton states to contribute to the SiNC EL. In fluorescent OLEDs, the increase in spin fraction could happen via several possible mechanisms, for example: thermally activated delayed fluorescence (TADF) [138, 139], triplet-triplet annihilation [140] and exciton transfer process [43, 141]. Details on theses mechanisms will be discussed later, and right now we will focus on accurately determining the value of exciton spin faction χ.

If we rearrange Equation (2.1), spin fraction χ can be written as follows:

$$\chi\gamma = \frac{\eta_{EQE}}{\eta_{PL}\eta_{OC}} \quad (6.4)$$

Following the discussions earlier, the device η_{EQE} has a peak value of 8.6% [34]. And if we further take η_{PL} as 40%, η_{OC} as ~20% and γ as unity due to mobility balance in our 1:5 SiNC-OLEDs, the calculated χ is close to 1, suggesting that almost every exciton generated in SiNC-OLEDs could contribute to the radiative recombination. This estimation is surprising. Thus, experiments that can accurately measure the spin fraction definitely need to be conducted.

Segal et al. developed a method to measure the upper limit of the excitonic statistics in fluorescent OLEDs [137], which could also be utilized to probe the spin fraction in SiNC-OLEDs. The experimental setup is shown in Figure 6.2. A 405 nm CW laser is employed to excite the device. The laser beam is right aligned with device cathode. The excited PL is collected by a silicon photodiode after passing through a 450 nm colored

glass filter. Under reverse bias, the PL intensity will be quenched by a certain amount because the applied electrical field could dissociate some generated excitons into charges. Assuming k_e, the quenching rate of excitons due to electrical field, is small and independent of field, ΔP_{PL}, the differential PL power, is given by:

$$\Delta P_{PL} = P_{PL}(k_e) - P_{PL}(k_e = 0) = -\eta_{OC} h\nu \frac{k_e}{k_r + k_{nr}} \phi \tag{6.5}$$

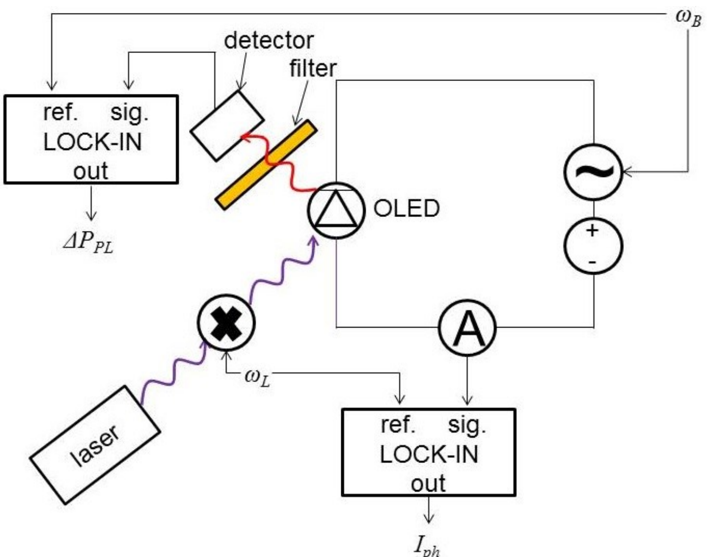

Figure 6.2 Testing geometry of two-tone synchronous spin fraction measurement.

In this equation, v is the frequency of emitted photons in SiNC layer, and Φ is the photon flux. Meanwhile, the charges that are formed from the dissociated excitons could also be measured. The generated photocurrent, I_{ph}, can thus be written as equation 6.6.

$$I_{ph} = e \frac{k_e}{k_r + k_{nr}} \phi \tag{6.6}$$

Combing Equation (6.4) to (6.6), we can obtain:

$$\eta_{OC} \eta_{PL} = -\frac{e}{h\nu} \frac{\Delta P_{PL}}{I_{ph}} \tag{6.7}$$

The key of this method is that both EL and PL are tested in the same geometry, so that the out-coupling efficiency, η_{OC}, which is often difficult to measure, could be

canceled out, and from which an expression for spin fraction χ, can be reached as in Equation (6.8). Here P_{EL} and I_{inj} are the EL power and injected current at forward bias with the same setup.

$$\chi = \frac{\eta_{EQE}}{\eta_{OC}\eta_{PL}\gamma} = \frac{P_{EL}}{I_{inj}} \Big/ \frac{-\Delta P_{PL}}{I_{ph}} \tag{6.8}$$

Preliminary measurement on spin fraction had already been done by Dr. Kai-Yuan Cheng in our group before. However, as the hole transport material (poly-TPD) had a bandgap of 2.8 eV, which could absorb significantly amount of incident laser photons, Dr. Cheng simply removed that layer and conducted the experiment at DC bias. Assuming a unity value for γ, the corresponding χ was estimated to be ~56%.

Although this number is lower than the calculated value previously, it proves that more than 25% of the total excitons could radiate in our SiNC-OLEDs. But there are still two problems associated with his experiment. First, the device efficiency is not optimized because of lack of hole transport layer. Thus γ may deviate significantly from unity. Second, leakage current under reverse bias is not taken into consideration. This will lead to an overestimation of photocurrent.

To solve the first problem, a new device structure is proposed. Here we will use Poly(9-vinylcarbazole), or PVK, to replace low bandgap hole transport material poly-TPD, which helps confine the excitons in the SiNC layer without absorbing 405 nm laser photons. The energy band diagram is shown in Figure 6.3. However, PVK is known to be redissolved by chloroform when spin-coating SiNC solution, so that device performance is poor [36]. To prevent redissolving, we propose to insert a thin layer of wide bandgap optically transparent Nickel Oxide (NiO) in the middle. The matched energy levels and

much higher mobility will not greatly shift the exciton recombination zone, so that high EQE could still be achieved.

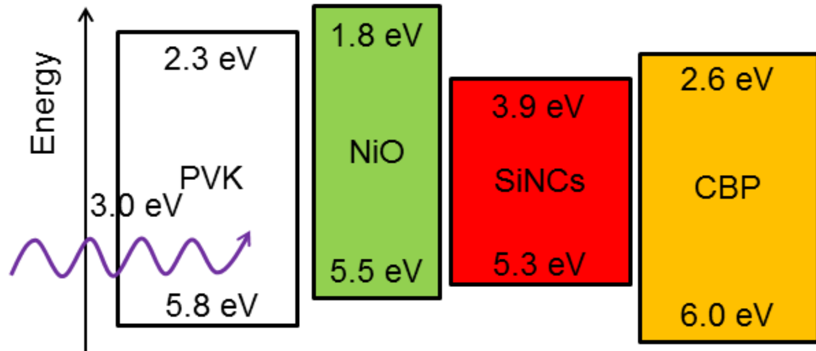

Figure 6.3 Energy band diagram of proposed device structure for spin fraction measurement.

The leakage current at reverse DC bias could be screened out with the two-tone synchronous measurement setup as shown in Figure 6.2. The 405 nm CW laser is cut by a mechanical chopper with frequency ω_L, which also serves as a reference signal to measure photocurrent. Using a lock-in amplifier, the leakage current, which is in frequency ω_B, will be discarded. Similarly, the voltage source working at frequency ω_B, can also be used as a reference for the optical power. This experiment allows accurately probing the spin fraction in SiNCs.

6.3.2 Possible Mechanisms for High Spin Fraction

One possible mechanism that can raise the excitonic spin fraction up to unity is thermally activated delayed fluorescence (TADF), through which the lower energy triplet (T_1) excitons can absorb a phonon from ambient and upconvert into higher energy singlets (S_1). This process, so-called reverse intersystem crossing (RISC), can be better understood with the help of Figure 6.4. For a material with small energy difference (ΔE_{ST})

between S_1 and T_1 states, it is possible that the room ambient phonons could supply enough energy and momentum at the same time, which greatly facilitates this RISC transition. The non-radiative triplet excitons can thus be transformed into radiative singlets, and the total spin fraction χ is increased.

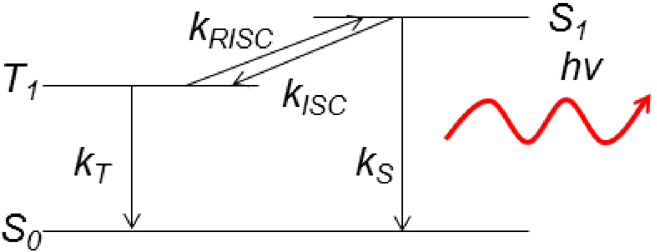

Figure 6.4 Schematic plot of thermally activated delayed fluorescence (TADF). S_0 is the ground state. T_1 and S_1 stand for triplet and singlet excited states; k_t and k_s represent triplet and single decay rates. k_{ISC} and k_{RISC} are inter-system crossing (ISC) and reverse intersystem crossing (RISC) rates, respectively.

In organic semiconductors, RISC is usually considered as a forbidden process. For instance, in the most frequently used phosphorescent chemical, Tris[2-phenylpyridinato-C2,N]iridium(III) ($Ir(ppy)_3$), the energy difference between S_1 and T_1 state (ΔE_{ST}) is about 850 meV [142]. The energy is much higher than room temperature phonon energy (25 meV) such that the phonon–assisted upconversion process becomes very unlikely.

However, TADF has recently been discovered in organic semiconductors (2,4,5,6-tetrakis(carbazol-9-yl)-1,3-dicyanobenzene (4CzIPN) [139] and 4,4',4"-Tris(N-3-methylphenyl-N-phenylamino)triphenylamine: 2-(4′-biphenyl)-5-4″-tert-butylphenyl)-1,3,4-oxadiazole mixture (m-MTDATA:t-Bu-PBD) [138] through carefully designing and modifying the energy levels. The OLEDs which utilized this mechanism reveal an EQE over 5%, the upper limit of common fluorescent OLEDs. The transient PL of this chemical, reveals a clear bi-exponential decay, with the precoefficient for the faster decay

component changing with temperature. This precoefficient also varies when the material is electrical excited instead of using laser pulse, as shown in Figure 6.5.

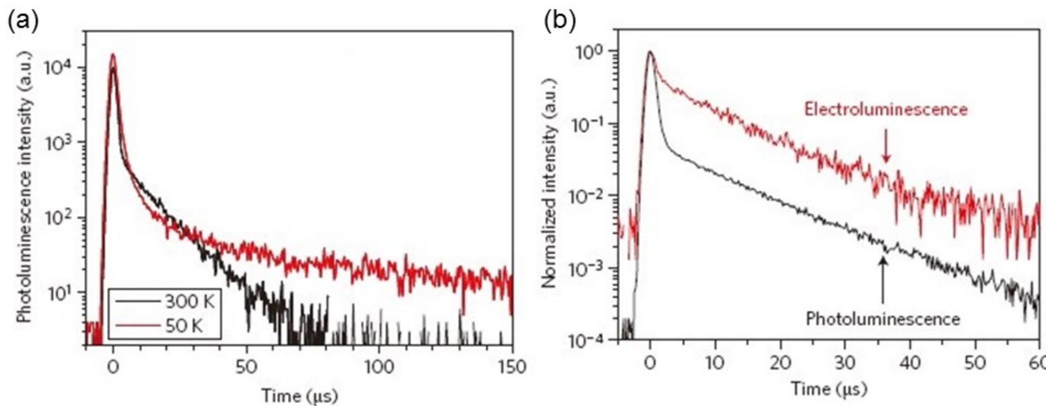

Figure 6.5 Transient decay of 50 mol% m-MTDATA:t-Bu-PBD film. **(a)** transient PL at 300 K (black) and 50 K (red) and **(b)** comparison of PL (black) and EL (red) transient decay curve at 300 K. (Reprinted from [138])

While it is also possible for this process to happen in NC-OLEDs, no solid proof has been given. In CdSe NCs [60, 62] and porous Si [143], temperature dependent transient PL study have been conducted to support TADF mechanism. However, the authors to those papers simple take the total lifetime τ as radiative lifetime τ_r (in other words, assuming a unity value for η_{PL}), which is problematic. Additionally, steady-state PL and transient EL experiments are in lack to validate TADF.

As argued earlier in this section, if the ambient phonon energy becomes not enough to support RISC at low temperature, integrated PL intensity will decrease significantly. However, within the temperature range (78 K to 296 K) in our PL experiments, this effect has not been observed. One possible reason is that (ΔE_{ST}) is typically smaller than 5 meV (corresponding to phonon energy at ~50 K) for SiNCs or porous Si [143]. To tell whether TADF happens or not, liquid Helium (~4 K) could be used for a complete temperature dependent PL and EL study.

Using the TADF schematic plot as shown in Figure 6.6, we are able to model the transient PL/EL decay process using Equation set (6.9) as shown below:

$$\begin{cases} \frac{dS_1}{dt} = R_1 - k_s S_1 - k_{ISC} S_1 + k_{RISC} T_1 \\ \frac{dT_1}{dt} = R_2 - k_T T_1 - k_{RISC} T_1 + k_{ISC} S_1 \end{cases} \quad (6.9)$$

In this equation set, R_1 and R_2 are the pump rate for S_1 and T_1 states, which become zero after the initial pulse. Solving Equation (6.9) will give the result as following:

$$\frac{d^2 S_1}{dt^2} + (k_S + k_{ISC} + k_T + k_{RISC}) \frac{dS_1}{dt} + (k_S k_T + k_s k_{RISC} + k_T k_{ISC}) S_1 = 0 \quad (6.10)$$

$$S_1(t) = A exp(-t/t_1) + (1 - A) exp(-t/t_2) \quad (6.11)$$

$$t_{1,2}^{-1} = \frac{k_S + k_T + k_{ISC} + k_{RISC} \pm \sqrt{(k_S + k_T + k_{ISC} + k_{RISC})^2 - 4(k_S k_{RISC} + k_T k_{ISC} + k_T k_S)}}{2} \quad (6.12)$$

Here $t_{1,2}^{-1}$ are the two Eigen roots of Equation (6.10). If we choose $t_1 < t_2$, A is precoefficient for the faster decay. These three terms could be obtained by fitting the transient decay curve $S_1(t)$ with a bi-exponential.

To characterize the temperature dependence, we assume that the RISC process is thermally activated, the rate of which follows:

$$k_{RISC} = \begin{cases} k_{ISC} & \Delta E_{ST} < k_B T \\ k_{ISC} \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right) & \Delta E_{ST} \geq k_B T \end{cases} \quad (6.13)$$

Note that ISC in organic semiconductors is usually a much faster process than singlet or triplet decay [99]. So at high temperature where $\Delta E_{ST} \geqslant k_B T$, S_1 and T_1 states will essentially mix and the transient decay curve should reduce to a single exponential, as showed previously in Chapter 5.

In addition, boundary conditions of T_1 should also be considered, as displayed in Equation (6.14). Combining Equation (6.9) to (6.14) could allow fitting for the value for ΔE_{ST}.

$$T_1(0) = -\frac{A}{t_1} - \frac{1-A}{t_2} + k_S + k_{ISC} = 0\ (PL) or\ 3\ (EL) \quad (6.14)$$

To sum this section, future work on temperature dependent transient PL and EL study will be helpful to determine whether TADF is the mechanism for high spin fraction in our SiNC-OLEDs.

6.4 Energy Transfer in Silicon Nanocrystals

Energy transfer process is an important process that impacts on exciton spin fraction in OLEDs [91, 135] and NC-OLEDs [43]. In phosphorescent OLEDs, such process is a necessary requirement to reach nearly unity spin fraction [136]. In term of CdSe NCs, evidence has also been given for possible exciton transfer from phosphors [47].

There are mainly two types of energy transfer process in organic semiconductors, Förster energy transfer [144] and Dexter energy transfer [145]. The former depends significantly on the spectral overlap between absorption and emission. This process is based on the Coulombic interaction, or dipole-dipole mediated mechanism, as shown in Figure 6.6 (a). It can be easily understood as transition of energy between donor and acceptor, but without emission of photon. Dexter energy transfer, on the other hand, is a short-ranged process, which depends on the collision of electron clouds. For this process to happen, significant overlap of electron clouds of donor and acceptor in real space is required, as envisioned in Figure 6.6 (b). Note that the effective range is 5 ~ 10 nm for

Förster process but only ~ 1 nm for Dexter process. So at long range, Dexter process is frequently ignored [146].

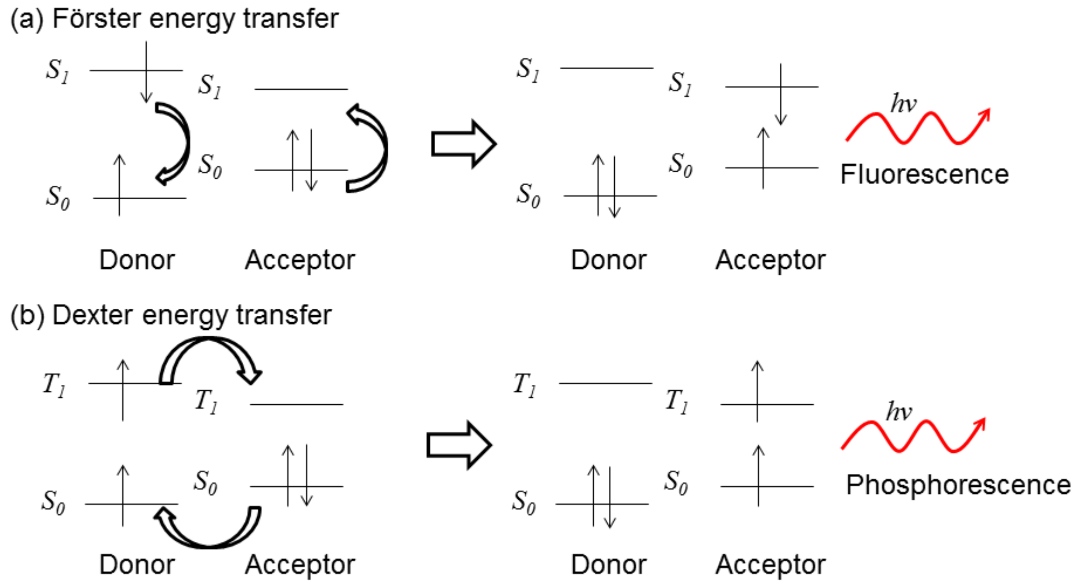

Figure 6.8 Schematic diagram of two energy transfer processes: **(a)** Förster energy transfer and **(b)** Dexter energy transfer. The arrows represent electrons with spin direction either upward or downward.

Here we are interested to explore whether such process happens or even is responsible for the high spin fraction in our SiNC-OLEDs or not. In our previous design using Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, with a 2.1 eV bandgap) as hole transport material, due to little spectral overlap between SiNCs absorption and MEH-PPV emission, exciton transfer is very unlikely [33]. But the situation becomes different for poly-TPD (bandgap 2.8 eV) [34]. The spectral overlap is greatly enhanced thus the possibility of exciton transfer cannot be ignored.

It should be mentioned that in some conjugated polymer semiconductors, probably due to electron and hole exchange interaction, exciton spin fraction is shown to be higher

than the 25% limit [141]. If it is also true for poly-TPD, spin fraction of our SiNC-OLEDs could also be affected.

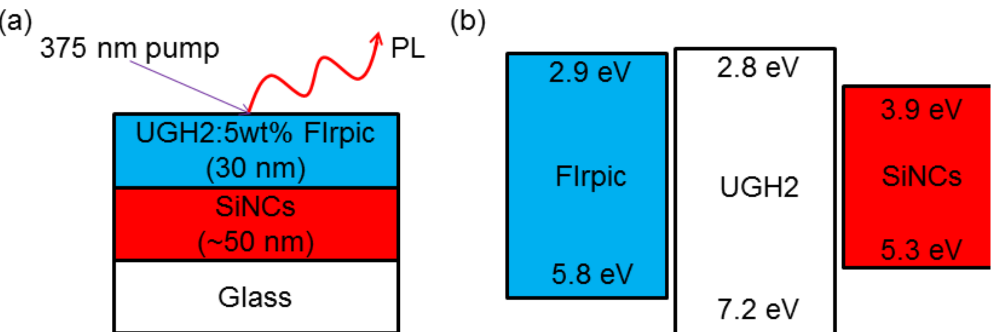

Figure 6.7 (a) Proposed PL quenching geometry and **(b)** energy levels of materials involved in the PL quenching experiment.

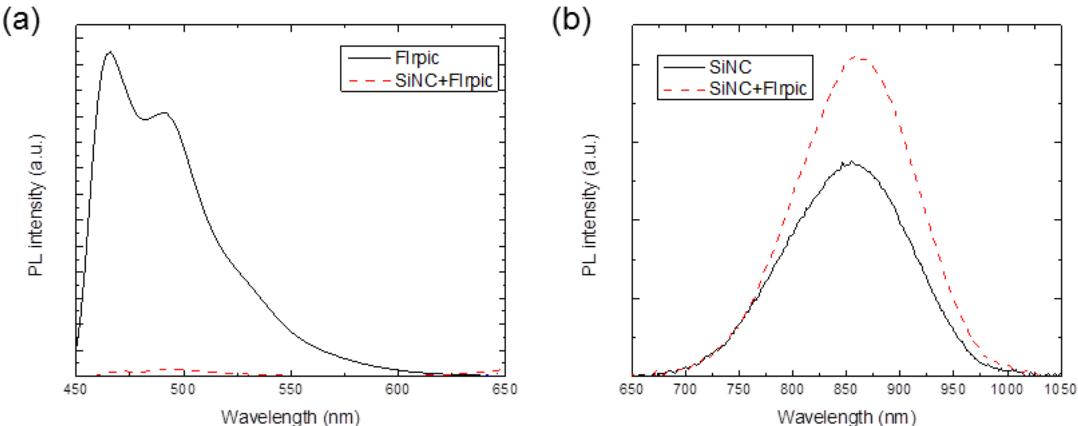

Figure 6.8 (a) Comparison of pure FIrpic (black solid) and SiNC+FIrpic (red dash) PL spectra. **(b)** Comparison of pure SiNC (black solid) and SiNC+FIrpic (red dash) PL spectra.

To test existence of exciton transfer in SiNCs, for an initial try, we design a PL quenching experiment as shown in Figure 6.7 (a). Bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium(III) (FIrpic) is selected because it demonstrates a similar bandgap (2.9 eV) with poly-TPD but with much higher η_{PL} (~ 90%, instead of 10%). Interestingly, we find that when SiNCs layer is deposited underneath FIrpic, the emission due to FIrpic is greatly quenched. Meanwhile, compared to pure SiNC, emission in the

near infrared spectrum is significantly enhanced when FIrpic is used, as shown in Figure 6.8. This trial suggests that exciton transfer may happen efficiently between FIrpic and SiNCs.

In order to model this process, we follow the model described in [146]. We here consider only Förster process since Dexter process is short-ranged. The effective transfer range, or Förster radius R_0, is given by Equation (6.15) [99]:

$$R_0^6 = \frac{9\eta_{PL}\kappa^2}{128\pi^5 n^4}\int \lambda^4 F_d(\lambda)\sigma_A(\lambda)d\lambda \tag{6.15}$$

In this equation, κ is the dipole orientation factor and n is the refractive index. $F_d(\lambda)$ and $\sigma_A(\lambda)$ stand for the normalized donor emission and acceptor absorption cross-section spectra, respectively.

In a thick quenching layer geometry, the exciton transfer rate, $k_F(d)$, is given by Equation (6.16) [147]:

$$k_F(d) = \frac{\rho_A}{\tau}\frac{\pi R_0^6}{6d^3} \tag{6.16}$$

Where ρ_A is the molecular density of acceptor, τ is exciton lifetime and d is the distance between donor and acceptor.

Taking exciton transfer as an additional term in one dimension diffusion equation, we can thus have:

$$D\frac{d^2n(x)}{dx^2} - \frac{n(x)}{\tau} + \frac{Q(x)}{h\nu} - n(x)k_F(d) = 0 \tag{6.17}$$

In Equation (6.17), D is the diffusion coefficient, $n(x)$ is the concentration function, and $Q(x)$ is the generation profile of excitons. We can easily change the donor-acceptor distance, d, by inserting an optical transparent layer, triphenyl-(4-triphenylsilylphenyl)silane (UGH2, bandgap 4.4 eV), in the middle, as shown in Figure

6.9 (b). This allows numerically fitting for Förster radius R_0. A large value of R_0 could suggest efficient energy transfer. Experiment with poly-TPD and SiNCs will be conducted later.

6.5 Afterword

In the last two decades, significant improvement on device efficiency in NC-OLEDs has been made. We hope that through this study, electrical and optical properties of SiNCs could be connected adequately to their device performance. Of course, more research is needed to be done to elucidate the exciton spin fraction in SiNCs, and to realize of long-lifetime and full-color-display for future commercialization. This work may serve as a useful guidance to help select and synthesize proper NCs, and design highly efficient NC based optoelectronic devices in the future.

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Appendix:

A.1 Structures of the Chemicals Mentioned in This Thesis

Short name	Full name	Chemical structure
PPV	poly-(para-phenylenevinylene)	n
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate)	O O S SO_3H
poly-TPD	poly(4-butylphenyl-diphenyl-amine) (poly-TPD)	N n
Alq_3	tris(8-hydroxyquinolinato) aluminum	N O O Al N O N

TCTA	4,4',4''-tris-(N-carbazolyl)-triphenlyamine	
CBP	4,4′-Bis(*N*-carbazolyl)-1,1′-biphenyl	
PVK	Poly(9-vinylcarbazole)	
$Ir(ppy)_3$	Tris[2-phenylpyridinato-C^2,N]iridium(III)	
4CzIPN	(2,4,5,6-tetrakis(carbazol-9-yl)-1,3-dicyanobenzene	

m-MTDATA	4,4',4''-Tris(N-3-methylphenyl-N-phenylamino)triphenylamine	
t-Bu-PBD	2-(4′-biphenyl)-5-4″-tert-butylphenyl)-1,3,4-oxadiazole	
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]	
FIrpic	Bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium(III)	
UGH2	triphenyl-(4-triphenylsilylphenyl)silane	