

# Dual-emission of silicon quantum dots modified by 9-ethylanthracene†

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Cite this: *J. Mater. Chem. C*, 2014, 2, 1977Received 25th November 2013  
Accepted 25th December 2013

DOI: 10.1039/c3tc32318h

www.rsc.org/MaterialsC

Silicon quantum dots (QDs) have attracted much interest in recent years for their prospects in biology and opto-electronics; also, anthracene is a star material for being the first organic molecule to be used in an electroluminescence (EL) device. In this paper, we report dual-emissive Si QDs, with the QD surface modified by 9-ethylanthracene. This hybrid nanomaterial dispersed well in nonpolar solvents such as mesitylene, exhibiting a dual-emission spectrum with peaks centered at 431 and 824 nm, corresponding to the ligand and Si QD related fluorescence, respectively. This is a general strategy for preparing dual-emission Si QDs with wavelengths tunable either by the size of the Si nanocrystals or by the molecules. This dual-emissive hybrid nanomaterial exhibits possible application potential as an active material for visible to near infrared light emitting devices or bio-imaging.

## Introduction

Semiconductor quantum dots, as a fascinating species of inorganic compounds, have a wide range of applications due to their attractive electronic and optical properties, such as tunable fluorescence with a high-quantum yield, a broad absorption window and a narrow fluorescent wavelength compared to organic molecules.<sup>1,2</sup> However, many semiconductor compounds have been found to be toxic and environmentally harmful, which limits the use of these compounds.<sup>3–5</sup> As a unique branch of semiconductor quantum dots, group IV semiconductor silicon is environmentally friendly and inexpensive in comparison with traditional II–VI (*e.g.*, CdX, X = S, Se, Te) and III–V (*e.g.*, InAs, InP) semiconductor materials.<sup>3</sup> Si QDs also find application in optoelectronics, solar energy conversion, biologic sensors, photo detectors, *etc.*<sup>6,7</sup> Therefore, the synthesis of functional Si QDs has attracted increasing attention in the past decade. A variety of chemical and physical routes have been reported for the preparation of Si QDs,<sup>8,9</sup> such as reduction of SiCl<sub>4</sub> in solution with reducing agents,<sup>9–14</sup> the metathesis reaction between sodium silicide and NH<sub>4</sub>Br,<sup>12,15</sup> the annealing of SiO<sub>x</sub> powders followed by etching with HF,<sup>16,17</sup> electrochemical etching of silicon wafers,<sup>18</sup> plasma synthesis or plasma-enhanced chemical vapor deposition (PECVD)<sup>19</sup> and high temperature hydrogen reduction.<sup>20–23</sup> To achieve stability against oxidization and to enhance the dispersibility of Si QDs in organic or aqueous solutions, alkyl chains with –CH<sub>3</sub>, –COOH or –NH<sub>2</sub> ends have been applied to the surface modification of Si QDs.<sup>2b</sup> Furthermore, although opto-electronic functional organic

molecules have been widely used in many fields, they have seldom been employed as ligands of Si QDs so far. From this perspective, anthracene and its derivatives came to our attention. In the 1960s, Pope and Kallmann developed ohmic dark-injecting electrode contacts with a single crystal of anthracene.<sup>24</sup> This achievement promoted the development of OLED devices. Latterly, high-efficient electroluminescence devices based on anthracene derivatives have been developed.<sup>25–27</sup> In this report, we explored the synthesis and surface modification of Si QDs with 9-ethylanthracene, using hydrogen terminated Si QDs and 9-vinylanthracene as the starting materials. The material was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy. Interestingly, the 9-ethylanthracene modified Si QDs (referred as '9-*ea*-Si QDs' for short) exhibit dual-emission in the photoluminescence spectrum, with peaks centered at 431 and 824 nm, corresponding to the ligand and Si QD related fluorescence, respectively. The PL spectrum and PL lifetime of 9-ethylanthracene bonded to Si QDs varies from that of the free anthracene or 9-vinylanthracene, suggesting a ligand to Si QD coupling effect. It is expected to be a potential material for visible to near infrared light emitting devices. Also, it is a general strategy for preparing dual-emission Si QDs with wavelengths tunable either by the size of Si nanocrystals or by the modified molecule structure.

## Experimental section

### Materials and methods

HSiCl<sub>3</sub> (99%) and mesitylene (97%) were purchased from Aladdin. 9-vinylanthracene (97%) was purchased from Alfa Aesar. Analytical grade ethanol (99.5%) and hydrofluoric acid

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3tc32318h

(40% aqueous solution) were received from Sinopharm. All reagents were used as purchased without further purification. The XRD was performed on a Bruker D8 Advance instrument with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The TEM image and EDX spectrum were obtained on a JEM-2100 transmission electron microscope with an acceleration voltage of 200 kV.

FTIR spectra were measured by a VECTOR 22 spectrometer with KBr pellets. The XPS spectrum was recorded by a PHI 5000 VersaProbe (U1VAC-PHI). The PL and PLE spectra were collected by a Hitachi F-4600 fluorescence spectrophotometer. The PL lifetime was obtained on a Zolix Omini- $\lambda$  300 fluorescence spectrophotometer.

### Synthesis of hydrogen terminated freestanding Si QDs

The Si QDs were synthesized by a hydrogen reduction route, which is similar to the previously reported method.<sup>20</sup> Typically, 5 mL of HSiCl<sub>3</sub> (6.7 g, 49.5 mmol) was added to a three-necked-flask with a magnetic stirrer bar and kept at  $-78 \text{ }^\circ\text{C}$  for 10 min, using standard Schlenk techniques with N<sub>2</sub> protection. Then 20 mL ( $\sim 1.1 \text{ mmol}$ ) of distilled water was injected with stirring. A lot of white precipitate and HCl gas were formed immediately. After 10 min, the precipitate was collected by centrifugation, washed with distilled water and dried under vacuum at  $60 \text{ }^\circ\text{C}$  overnight. The as prepared white powder (HSiO<sub>1.5</sub>)<sub>n</sub> was used for further reaction. The (HSiO<sub>1.5</sub>)<sub>n</sub> powder (1.10 g, 25 mmol) was placed in a corundum crucible and transferred to a tube furnace at room temperature. Then the temperature was ramped to  $1150 \text{ }^\circ\text{C}$  at a speed of  $5 \text{ }^\circ\text{C min}^{-1}$  and maintained for 2 h under a slightly reducing atmosphere containing 5% H<sub>2</sub> and 95% Ar ( $\geq 99.999\%$ ). After cooling to room temperature, a light brown product of a Si/SiO<sub>2</sub> composite was collected. Prior to etching, grinding of the composite in a mortar and pestle was performed for 10 min. The ground Si/SiO<sub>2</sub> products (0.10 g) were transferred to a Teflon container (20 mL) with a magnetic stirrer bar. A mixture of ethanol (3 mL) and hydrofluoric acid (40%, 5 mL) were added. The light brown mixture was stirred for 60 min in order to dissolve the SiO<sub>2</sub>. Finally, 10 mL of mesitylene was added to extract the hydrogen terminated Si QDs into the upper organic phase, forming a cloudy brown suspension (A), which was isolated and saved for further surface modification.

### Modification of Si QDs by photoluminescent organic ligands

A mixture of 15 mL of mesitylene dissolved 9-vinylanthracene (0.20 g, 0.98 mmol) was loaded in a 50 mL three-neck-flask equipped with a reflux condenser. Then 2 mL of Si QDs (A) was added. The solution was degassed by a vacuum pump for 10 min. Protected by nitrogen, the solution was heated to  $156 \text{ }^\circ\text{C}$  and kept for 12 hours. After cooling to room temperature, the resulting Si QDs were purified by vacuum distillation to removed excess solvent and organic ligands. The as prepared brown solid product was washed with ethanol and then re-dispersed in mesitylene to give a yellow solution.

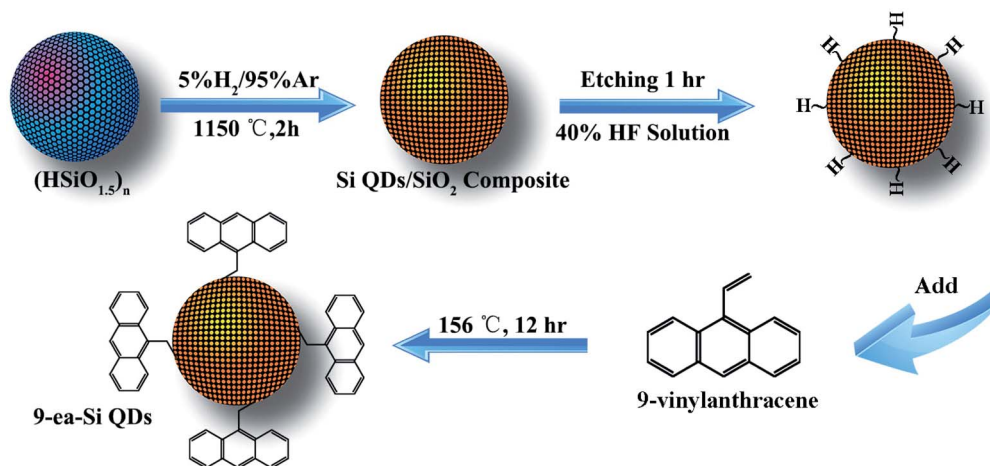
## Results and discussion

Scheme 1 shows the synthetic strategy of 9-*ea*-Si QDs. The HF etching procedure eliminates the SiO<sub>2</sub> component, liberating

the hydrogen terminated free Si QDs, which can react with terminal alkenes (9-vinylanthracene in this report) to form a Si–C bond. The XRD pattern of the hydrogen terminated Si QDs (Fig. 1a) is in good agreement with the fcc structured Si crystal (pdf no. 895012). The  $2\theta$  peaks at around  $28^\circ$ ,  $47^\circ$ ,  $56^\circ$  are readily indexed to the (111), (220) and (311) crystal planes. The broad full-width-at-half-maximum (FWHM) indicates the very small size of the Si nanocrystals. Fig. 1b shows a typical high-resolution transmission electron microscopy (HRTEM) image of the 9-*ea*-Si QDs. The average diameter of the 9-*ea*-Si QDs is about 5.4 nm (Fig. 1b, inset), determined by HRTEM measurements, which is consistent with the value of 5.7 nm calculated from the XRD spectrum using the Scherrer equation. The average size of Si QDs can be controlled by the temperature and duration of the hydrogenous reduction. For example, Ozin *et al.* reported that 3.2 nm Si QDs can be prepared at  $1100 \text{ }^\circ\text{C}$  for 1 h.<sup>22</sup> We raised the temperature to  $1150 \text{ }^\circ\text{C}$  and extended the time to 2 h, resulting in Si QDs of increased size. The etching procedure also plays a key role in the size control of the Si QDs, for the HF etches not only the SiO<sub>2</sub> matrix but also the Si QDs, gradually.

The components and surface of the crude and surface modified Si QDs were characterized by FTIR spectroscopy (Fig. 1c), which clearly illustrates the steps in Scheme 1. Freshly after the hydrogen reduction, a strong Si–O–Si vibration band at  $1000\text{--}1200 \text{ cm}^{-1}$  of the crude product was recorded, indicating the presence of Si/SiO<sub>2</sub> composites.<sup>21</sup> After the etching procedure, the Si–O–Si vibration disappeared, while two new bands at  $2090 \text{ cm}^{-1}$  and  $906 \text{ cm}^{-1}$  were observed. These vibration resonances are assigned to the coupled H–Si–Si–H stretching and monohydride Si–H bonds, respectively.<sup>12d,28</sup> The IR spectrum of the solid 9-*ea*-Si QDs reveals clear C–H stretching ( $2858\text{--}2916 \text{ cm}^{-1}$ ) and bending ( $1442\text{--}1473 \text{ cm}^{-1}$ ) vibration bands, which are assigned to the surface-bonded 9-ethylanthracene (–C<sub>16</sub>H<sub>11</sub>) groups.<sup>22</sup> The intensity of Si–H stretching bands (at 2090 nm and 906 nm) vanishes, confirming the Si–H bond was replaced by the Si–C bond. The vibrations between  $1091$  and  $1208 \text{ cm}^{-1}$  possibly indicate the presence of limited nanocrystal surface oxidation,<sup>21,22</sup> which could be induced by the 9-ethylanthracene modification or the dry procedure in FTIR sample preparation. The broad peak near  $3500 \text{ cm}^{-1}$  is unambiguously assigned to the stretching vibration of the –OH group, which could originate from sample adsorption of H<sub>2</sub>O from the air, or from the reaction of the unpassivated Si atom on the nanocrystal surface with the adsorbed H<sub>2</sub>O forming Si–OH species. The latter is more likely in this situation, for the surface modified by 9-ethylanthracene would induce steric effects so that not all the Si surface can be passivated and also because of the high reactivity of the Si nanocrystal surface.

The 9-*ea*-Si QDs were also characterized by X-ray photoelectron spectroscopy (XPS). Using a Shirley background subtraction, the fitting curves are shown in Fig. 2. The XPS spectrum exhibits two strong fitted peaks centred at 99.1 eV and 99.7 eV, which are attributed to the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> spin-orbit of silicon in the nanocrystal core (Si<sup>0</sup>), respectively.<sup>22,29</sup> Si<sup>+4</sup> is attributed to the Si surface oxide; While species of Si<sup>+1</sup> and Si<sup>+3</sup> are attributed to Si–C bonding,<sup>29</sup> indicating covalent bonding between 9-ethylanthracene and the Si QDs.



Scheme 1 Synthetic strategy of 9-ea-Si QDs.

The photoluminescence properties of the 9-ea-Si QDs, 9-vinylanthracene and decane-capped Si QDs were measured in mesitylene solutions. The 9-ea-Si QDs and freestanding 9-vinylanthracene ligands show similar excitation spectra (Fig. 3a) with the peaks almost unchanged within the range of 270–420 nm, indicating the preservation of the anthracene chromophore after the modification reaction. Upon excitation at 360 nm, the 9-ea-Si QDs and freestanding 9-vinylanthracene show intense emission bands at *ca.* 431 nm and 441 nm, respectively (Fig. 3b). In comparison with freestanding 9-vinylanthracene, the ligand emission in the 9-ea-Si QDs exhibits a blue-shift of 10 nm. This remarkable shift is probably induced by the coordination effect between the Si QDs and 9-vinylanthracene. Generally, the interaction of molecular orbitals between a ligand and the central atom would induce a red shift. However, the vinyl group in 9-ethylanthracene transforms into an ethyl group during the hydrosilylation reaction, through which it is linked to the Si QD surface. This means that the conjugated structure of the molecule reduced from 9-vinylanthracene to anthracene. In addition, the ligand to QD bonding would enhance the structural rigidity of the ligand. All these reasons may contribute to the PL spectrum blue-shift. At the same time,

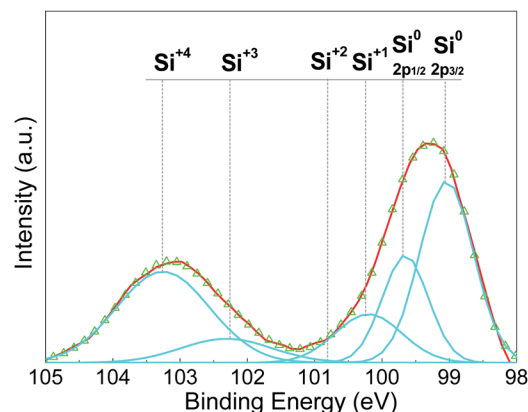
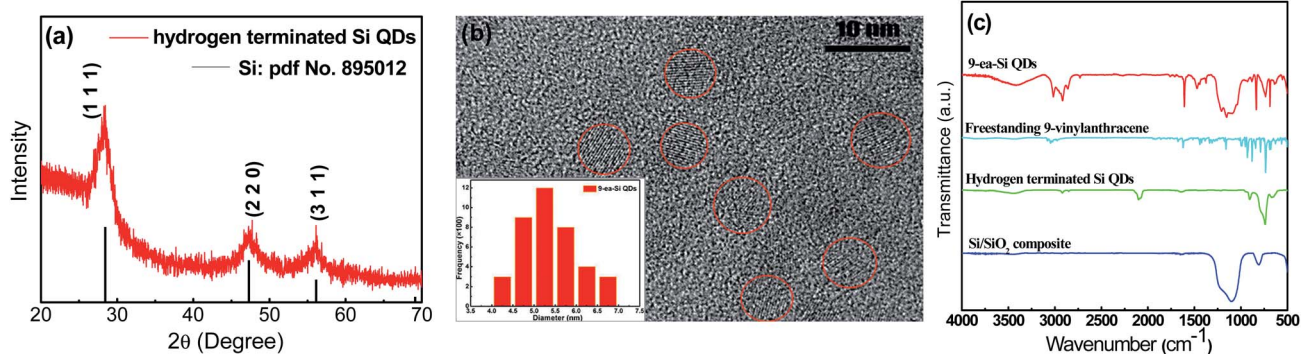


Fig. 2 Energy dispersive X-ray spectroscopy of 9-ea-Si QDs (green scatter: experimental data; red line: fitting curve; cyan line: spin-orbit partner lines).

the ethyl group formed through the hydrosilylation reaction separates the conjugated part, the anthracene, from the silicon nanocrystal, which prevents or weakens the interaction of the anthracene group with the electronic wave functions of the Si

Fig. 1 (a) XRD pattern of hydrogen terminated Si QDs; (b) HRTEM image of 9-ea-Si QDs. Scale bar: 10 nm; inset: size distribution of the 9-ea-Si QDs; (c) IR spectra of 9-ea-Si QDs, 9-vinylanthracene, hydrogen terminated Si QDs and Si/SiO<sub>2</sub> composites.



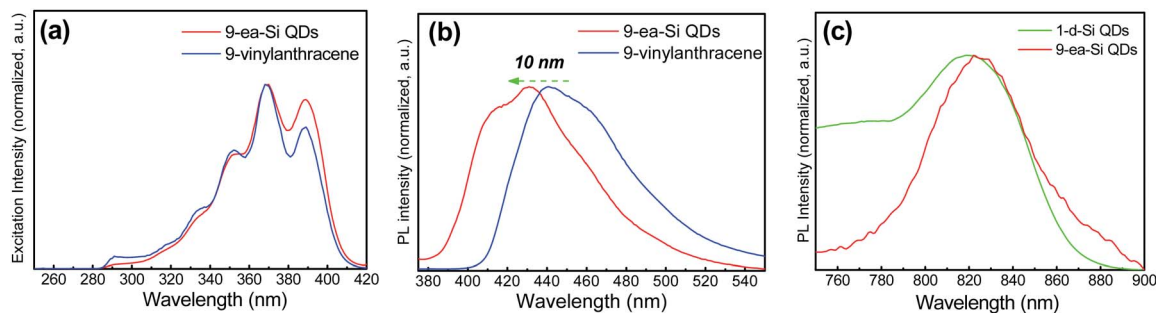


Fig. 3 (a) Excitation spectra of 9-ea-Si QDs and 9-vinylanthracene ligands in mesitylene at room temperature. Measured at emissions of 431 nm (9-ea-Si QDs) and 441 nm (9-vinylanthracene); (b) and (c) photoluminescence spectra of 9-ea-Si QDs, 9-vinylanthracene ligands and 1-d-Si QDs (excitation: 360 nm).

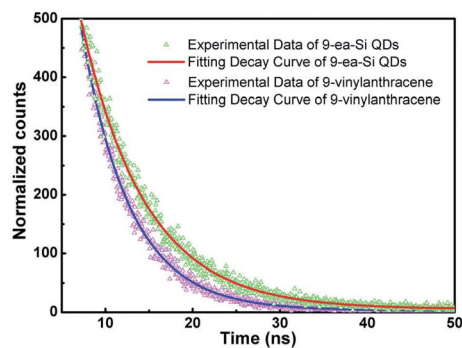


Fig. 4 PL decay curves of 9-ea-Si QDs measured at 430 nm and 9-vinylanthracene measured at 440 nm with excitation at 379 nm.

Table 1 The PL lifetimes

Sample	9-ea-Si QDs	9-vinylanthracene	Anthracene
$\tau$ (ns)	7.35	5.53	5.32 (ref. 30)

QDs. Therefore, a red shift is prohibited. Besides the ligand emission, a second emission peak at 824 nm was also observed, which is assigned to the intrinsic Si QD emission. To verify the origination of the near infrared emission, a parallel experiment was performed. 1-Decene was introduced instead of 9-vinylanthracene as the decorated group to passivate the surface of the Si QDs (forming 1-d-Si QDs), using a method similar to that of the 9-ea-Si QDs. A broad emission band centered at *ca.* 821 nm of the 1-d-Si QDs was observed (Fig. 3c), confirming the Si QD emission. Therefore, the 9-ea-Si QDs not only contain an emission band of the ligands but also preserve the photoluminescence of the Si QDs.

Fig. 4 shows the PL lifetime measurements of the 9-ea-Si QDs and 9-vinylanthracene in mesitylene. Both PL decay curves are well fitted to a single-exponential function:  $I(t) = A \exp(-t/\tau)$ , where  $A$  and  $\tau$  are the pre-exponential constant and the lifetime, respectively. Table 1 illustrates the fitting parameters. The PL lifetime of the 9-ea-Si QDs is 7.35 ns, which is longer than the PL lifetime of 9-vinylanthracene (5.53 ns) and anthracene (5.32 ns).<sup>30</sup> Various factors contribute to the life time diversity.<sup>31</sup>

The 9-vinylanthracene dispersion state in the mesitylene is not clear, oligomerization may possibly be induced by  $\pi$ - $\pi$  packing of the molecules, which could be supported by the fact that the ligand PL spectrum of the 9-ea-Si QDs is symmetric to the corresponding excitation spectrum, while 9-vinylanthracene shows an asymmetric feature; also the interaction of the molecule with the Si-QD is inevitably encountered; additionally, the hydro-silylation reaction induces the vinyl to ethyl transformation of the molecule structure. All of these would lead to lifetime modulation.

## Conclusions

In summary, dual-emissive 9-ea-Si QDs with fluorescence originating from both the organic modified ligands and inorganic Si QDs have been successfully synthesized. The strong Si-C bond provides the stability of the modification that is absent from ligand attaching-detaching equilibria in common colloidal nanocrystal solutions. The PL lifetime measurements reveal that the PL lifetime of the modified ligands of the 9-ea-Si QDs increases in comparison with free anthracene and 9-vinylanthracene. The strategy demonstrated in this report can be applied to functionalize Si QDs with various molecules with different properties. For example, the size controllable synthesis of the Si QDs together with the modified surface functional ligands can be utilized to enhance the absorption of pure Si QDs, therefore providing a potential strategy to increase the light-harvesting efficiency of Si QDs in solar cells.<sup>32</sup> The dual-emission feature of the single colloidal Si QDs is also applicable in bioimaging due to the bi-fluorescent channel that may be tuned from visible to near infrared.

## Acknowledgements

This work was supported by the Major State Basic Research Development Program of China (Grant no. 2013CB922102, 2011CB808704), the National Natural Science Foundation of China (Grant no. 91022031, 21301089) and Jiangsu Province Science Foundation for Youths (BK20130562). The authors gratefully acknowledge W. K. Duan and Prof. W. Wei for the PL lifetime measurement and Prof. X. Z. You for helpful discussion.

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