

Inverse quantum confinement in luminescent Silicon quantum dots

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Electron Dynamics in Complex Systems

ICAN26
Aachen
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1 Motivation

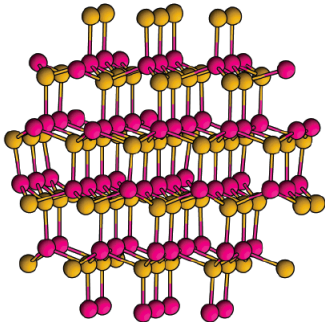
2 Theoretical Methods

- Time dependent DFT
- Approximate TDDFT $\Rightarrow$ TD-DFTB

3 Application to Silicon Nanostructures

- Hydrogenated SiQD - Simple and boring?
- Functionalization of Dots - Making them useful
- Surface reconstruction - Energetics and Spectra
- Silicon nanowires - Confinement in radial and axial dimensions

Quantum Dots - definition



CdS quantum dot

Characteristics

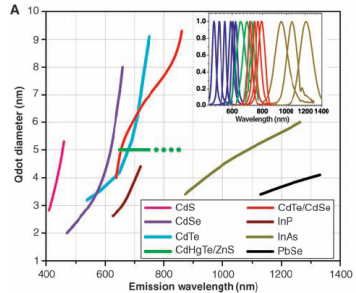
- An object that confines electrons in all three dimensions
- Made mostly from semiconductor material.
- Extension of nanometers
- Electronic level spacing comparable $k_B T$

Properties of Quantum Dots – Size dependent Emission



Fluorescence of Cadmium Selenide Quantum Dots

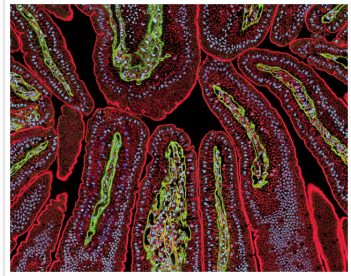
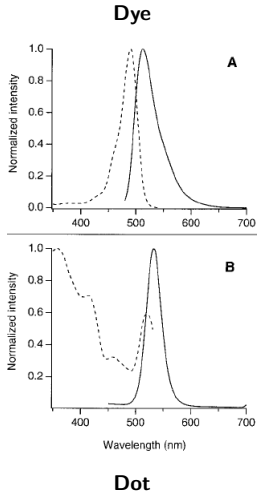
www.chemie.uni-hamburg.de/pc/weller/



Range of Emission Wavelength

Michalet Science (2005)

Properties of Quantum Dots – Advantages over Dyes

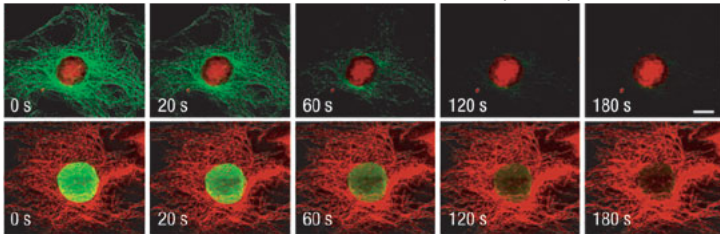


Mouse intestinal section
<http://probes.invitrogen.com>

Multi-color labelling
possible

Properties of Quantum Dots – Advantages over Dyes

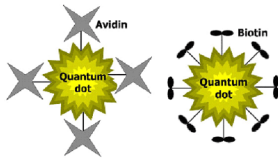
Medintz, Nature Materials (2005)



top: Nucleus labelled with Dot, microtubules with Dye
bottom: vice versa

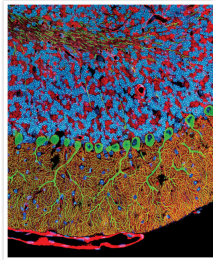
Quantum dots show only limited photobleaching

Quantum dots as markers in biology



Functionalization with
antibodies or aptamers

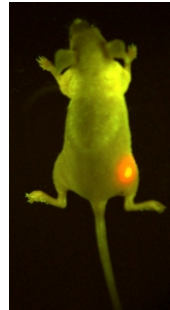
In vitro



Mouse cerebellum

<http://probes.invitrogen.com>

In vivo



Rat tumor

 Gao, Science (2004)

Probing the Cytotoxicity of Semiconductor Quantum Dots

Austin M. Derfus, Warren C. W. Chan,[†] and Sangeeta N. Bhatia*

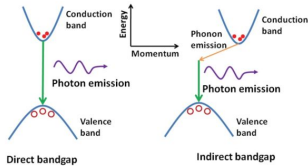
*Department of Bioengineering, University of California at San Diego,
La Jolla, California 92093*

Received September 3, 2003; Revised Manuscript Received November 7, 2003

ABSTRACT

With their bright, photostable fluorescence, semiconductor quantum dots (QDs) show promise as alternatives to organic dyes for biological labeling. Questions about their potential cytotoxicity, however, remain unanswered. While cytotoxicity of bulk cadmium selenide (CdSe) is well documented, a number of groups have suggested that CdSe QDs are cytocompatible, at least with some immortalized cell lines. Using primary hepatocytes as a liver model, we found that CdSe-core QDs were indeed acutely toxic under certain conditions. Specifically, we found that the cytotoxicity of QDs was modulated by processing parameters during synthesis, exposure to ultraviolet light, and surface coatings. Our data further suggest that cytotoxicity correlates with the liberation of free Cd²⁺ ions due to deterioration of the CdSe lattice. When appropriately coated, CdSe-core QDs can be rendered nontoxic and used to track cell migration and reorganization in vitro. Our results provide information for design criteria for the use of QDs in vitro and especially in vivo, where deterioration over time may occur.

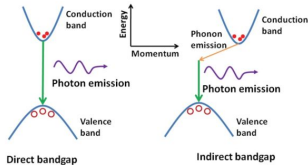
Silicon ???



Bulk Silicon

- phonon assisted emission
- fund. band gap of 1.13 eV

Silicon ???



Emission from SiH nanoparticles under UV excitation,  Belomoin, APL (2002)

Bulk Silicon

- phonon assisted emission
- fund. band gap of 1.13 eV

Silicon Quantum Dots

- Dipole-allowed transition
- Bright emission in the visible

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Time dependent Density Functional Theory

... describes the density evolution of a many electron system subject to a time dependent external potential

The time-dependent density of the **interacting** system of interest can be calculated as density

$$\rho(\mathbf{r}, t) = \sum_{i=1}^N |\phi_i(\mathbf{r}, t)|^2$$

of an auxiliary **noninteracting (KS)** system

$$i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left[-\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}, t) \right] \phi_i(\mathbf{r}, t)$$

with the **local** potential

$$v_{\text{KS}}[\rho](\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[\rho](\mathbf{r}, t)$$

Why is TDDFT useful?

Conventional DFT is only valid for the **groundstate**
Excited state properties are accessible within TDDFT

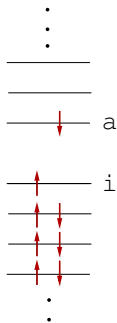
$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t) = \left[-\frac{1}{2}\nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}, t) \right] \phi_i(\mathbf{r}, t)$$

Perturbation theory

- ▶ Excitation energies
⇒ UV-Vis spectra
- ▶ Forces
⇒ Resonant Raman spectra
⇒ Luminescence
- ▶ Dipolemoments, Polarizabilities

Numerical solution

- ▶ Interaction with strong fields
- ▶ Follow electron dynamics in real time
- ▶ Nonadiabatic effects
- ▶ Molecular electronics



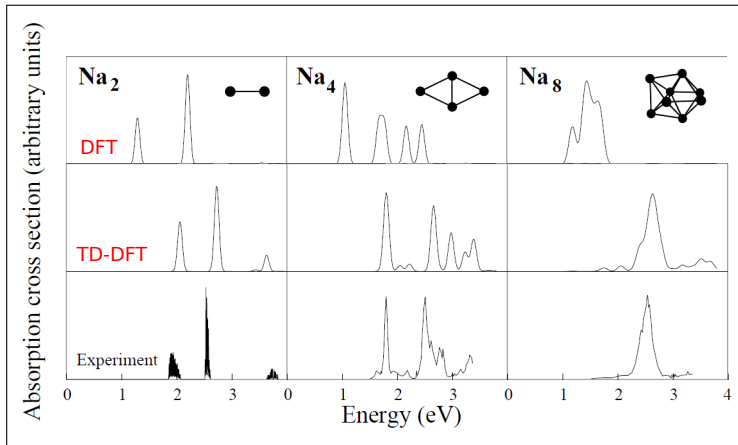
Equation to solve (Singlets):

$$\sum_{jb} [\omega_{ia}^2 \delta_{ij} \delta_{ab} + 2\sqrt{\omega_{ia}} K_{ia,jb} \sqrt{\omega_{jb}}] F_{jb}^I = \omega_I^2 F_{ia}^I$$

Couplingmatrix K leads to correction of single-particle picture

$$K_{ia,jb} = \iint' \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \right) \psi_j(\mathbf{r}') \psi_b(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

Light absorption of small metal clusters



 Vasiliev et al. – PRL **82** 1919 (1999)

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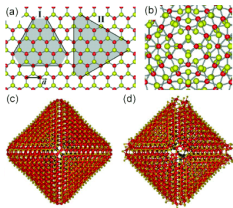
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Density functional based Tight-Binding (DFTB)

... is a simplified DFT method with additional approximations beyond the exchange-correlation functional.

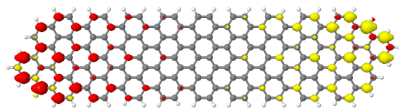
defects
large structures
many conformers
disordered systems
long MD

DFTB



DFTB-optimized structure of an $\text{Mo}_{576}\text{S}_{1140}$ fullerene (c), and the structure after an MD simulation at 300 K (d)

[15] A.N. Enyashin et al. – Ang. Chem. Int. Ed. **46** 623 (2006)



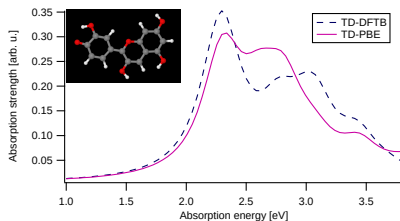
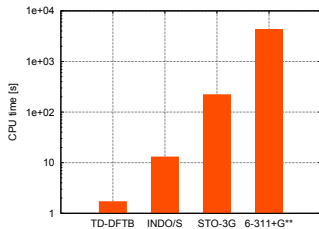
Spin-polarization of an armchair graphene nanoribbon with irregular edges

[16] C.-A. Palma, TAN et al. – JPC Letters **6** 3228 (2015)

Time dependent DFTB — TD-DFTB

Review:  TAN – Theochem **914** 38 (2009)

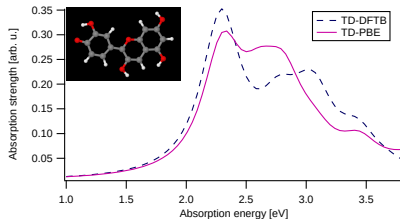
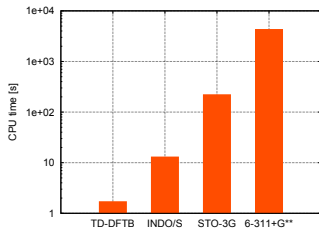
$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = H^{\text{DFTB}}\phi_i(\mathbf{r},t)$$



Time dependent DFTB — TD-DFTB

Review:  TAN – Theochem **914** 38 (2009)

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t) = H^{\text{DFTB}}\phi_i(\mathbf{r}, t)$$



Standard deviation from experiment (eV)

	TD-DFTB	TD-PBE	TD-B3LYP	TD-PM3
Sing. (21 Com.)	0.34	0.38	0.29	0.54
Trip. (12 Com.)	0.28	0.22	0.25	1.02

 F. Trani, G. Scalmani, G. Zheng, I. Carnimeo, M.J. Frisch, V. Barone – JCTC **7** 3304 (2011)

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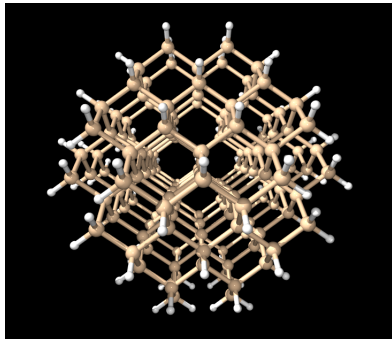
Prof. Rui-Qin Zhang
Xian Wang, Quan-Song Li, Chensheng Lin



Yong Wang



香港城市大學
City University
of Hong Kong



Model building

- ▶ Spherical bulk fragments Si_{1-199}
- ▶ H-passivation and relaxation
- ▶ Si-Si bonds 2.33-2.38 Å
- ▶ T_d symmetry
- ▶ $d(\text{Si}_5) = 0.45 \text{ nm}$ to $d(\text{Si}_{199}) = 2.0 \text{ nm}$

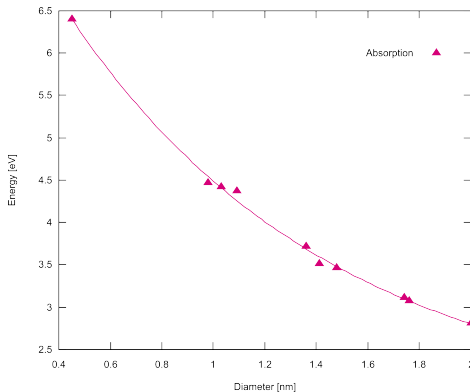
$S_1 - S_0$ energy [eV]

	DFTB	PBE	B3LYP	MR-MP2*	exp
SiH ₄	10.3	8.76	9.25		8.8
Si ₅ H ₁₂	6.40	6.09	6.66	6.56	6.5
Si ₂₉ H ₃₆	4.42	3.65	4.52	4.45	
Si ₃₅ H ₃₆	4.37	3.56	4.42	4.33	

* Garoufalidis, Zdetsis, Grimme, PRL **87** 276402 (2001)

B3LYP functional of choice for SiQD
DFTB is fine for larger dots

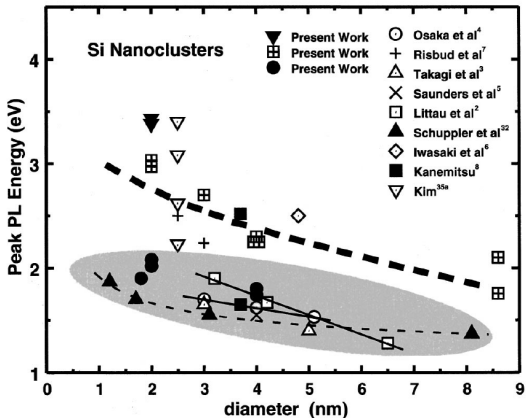
UV-Vis absorption energies of H-SiQD



Anticipated Particle-in-a-box behaviour

- X. Wang, R. Zhang, TAN, et al. – JPC C **111** 12588 (2007)
- X. Wang, R. Zhang, S.T. Lee, TAN, et al. – APL **90** 123116 (2007)

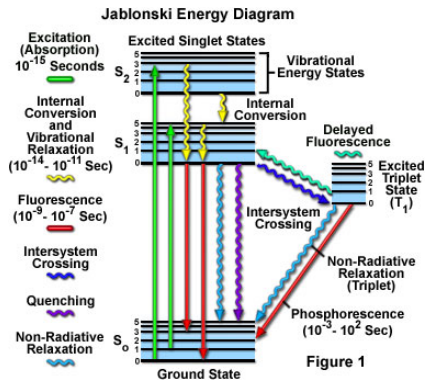
Experimental reports on SiQD photoluminescence



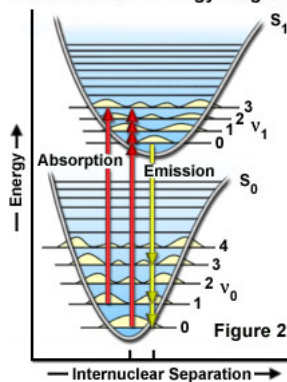
Peak PL versus Si nanocrystal size

 Wilcoxon et al. – PRB **60** 2704 (1999)

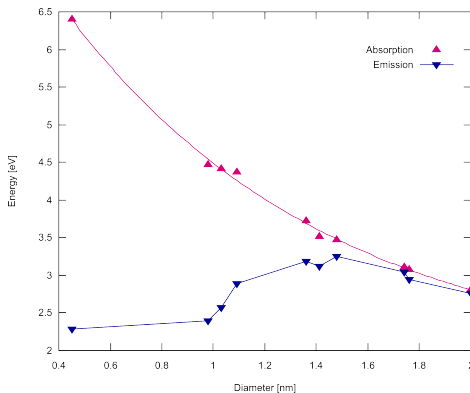
Luminescence and excited state processes



Franck-Condon Energy Diagram



Luminescence properties of H-SiQD

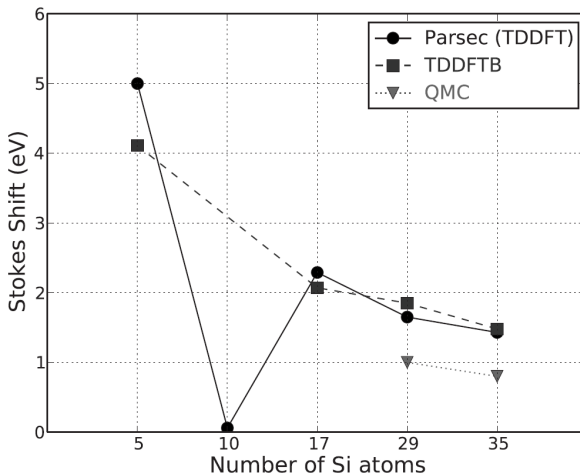


Huge Stokes shift for small particles

X. Wang, R. Zhang, TAN, et al. – JPC C **111** 12588 (2007)

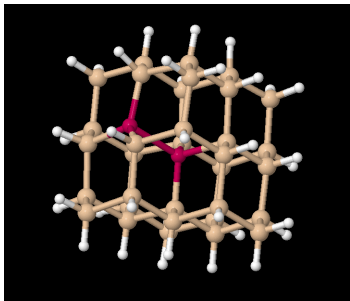
X. Wang, R. Zhang, S.T. Lee, TAN, et al. – APL **90** 123116 (2007)

Confirmation by *ab-initio* TDDFT

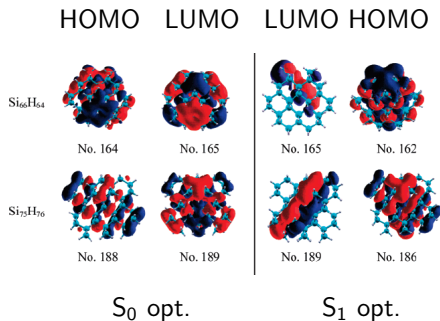


 Lopez del Puerto, Jain, Chelikowski – PRB **81** 035309 (2010)

Structure relaxation in the excited state



S_1 optimum of $\text{Si}_{35}\text{H}_{36}$



Formation of a self-trapped exciton

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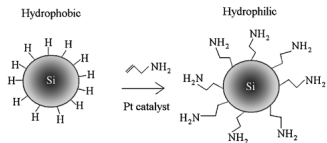
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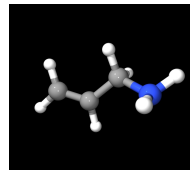
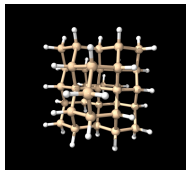
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Functionalization of dots



 Warner, *Angew. Chem.* (2005)

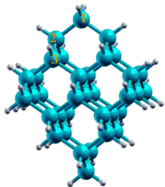


Functionalization with allylamine leads to

- ▶ Increased solubility
- ▶ Decreased aggregation
- ▶ Decreased oxidation

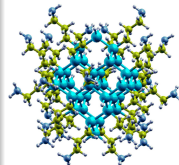
Does coating destroy the optical properties?

Generation of models



No preference in adsorption site

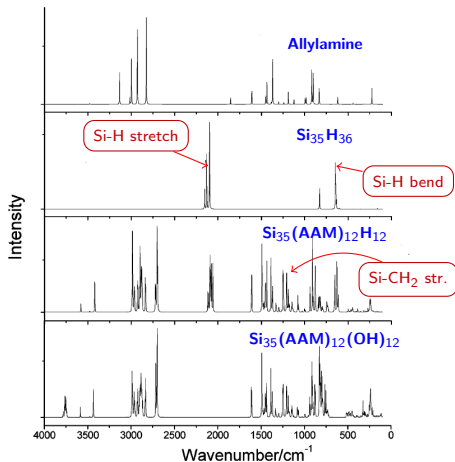
	Site	Binding energy [eV]
Si ₃₅ H ₃₆	1	2.44
	2	2.43
	3	2.44
Si ₅₉ H ₆₀	1	2.36
	2	2.44
	3	2.43



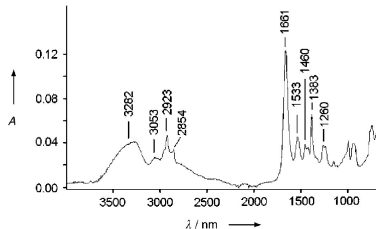
Complete coverage impossible

Wang, Zhang, TAN, Frauenheim, Lee, JPC C **111** 12588 (2007)

Simulated and experimental IR spectrum



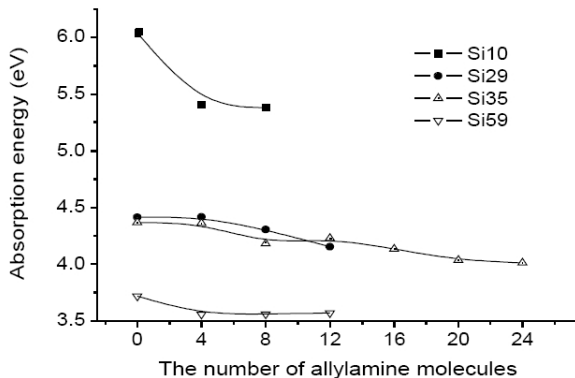
Partial oxidation?



Warner, Angew. Chem. **44** 4550 (2005)

Wang et al., JPC C **111** 12588 (2007)

TD-DFTB absorption energies



Strong quantum size effect – Little dependence on passivation

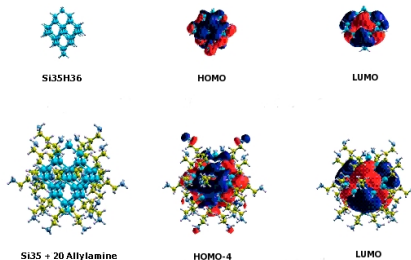
Maximum absorption and emission peaks

# Si	# allylamine	Absorption [nm]	Emission [nm]	Shift [nm]
10	0	205	421	216
29	0	281	405	124
35	0	284	429	145
	4	284	425	141
	8	297	462	165
	12	292	430	138
59	0	334	390	56
Exp.		320	480	160

Results

- ▶ Good agreement between exp. and theory for Si₃₅
- ▶ Red light emission requires larger dots as Si₅₉

Conclusions on allylamine functionalization



Allylamine is a promising candidate for protection and functionalization of Silicon quantum dots without perturbation of their favorable optical properties.

 Wang, Zhang, TAN, Frauenheim, Lee, JPC C **111** 12588 (2007)

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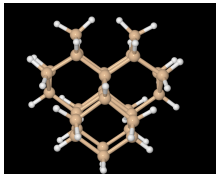
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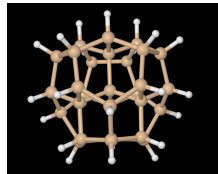
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Reconstructed Silicon Quantum Dots



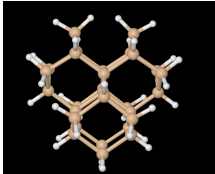
$\text{Si}_{29}\text{H}_{36}$

Dimer
formation by
 H_2
abstraction



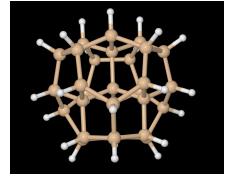
$\text{Si}_{29}\text{H}_{24}$

Reconstructed Silicon Quantum Dots

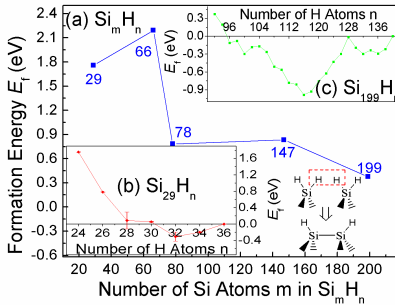


$\text{Si}_{29}\text{H}_{36}$

Dimer
formation by
 H_2
abstraction



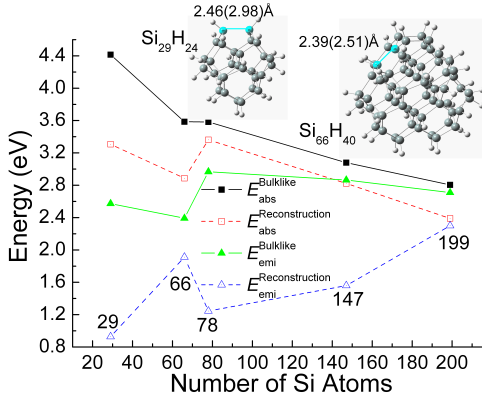
$\text{Si}_{29}\text{H}_{24}$



Formation energy:

$$E_f = E_{\text{re}} + (\Delta n/2)E_{\text{H}_2} - E_{\text{bl}}$$

Optical properties



Inverse quantum confinement effect

1 Motivation

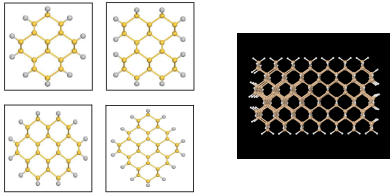
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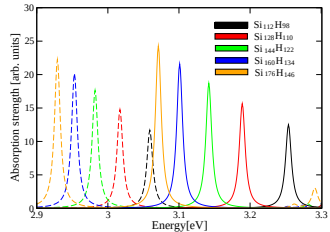
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Effects of confinement in radial and axial dimensions



Finite models of SiNW with [110]
growth direction



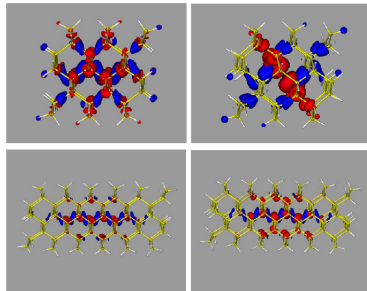
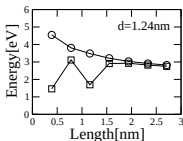
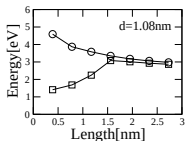
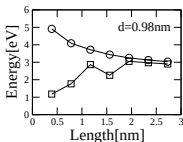
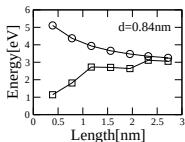
Absorption and emission spectra for
SiNW with $d = 0.84$ nm

Excited state relaxation does not quench
luminescence

Size dependence of exciton localization

HOMO and LUMO

$d=0.84$ nm and $l=1.17$ nm

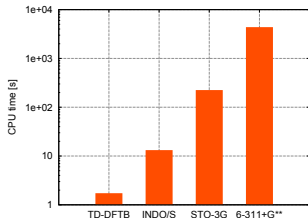


$d=0.84$ nm and $l=2.32$ nm

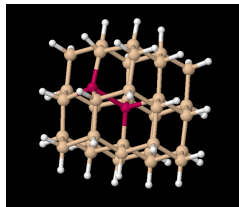
Exciton delocalizes for rods with $l > 2$ nm

Summary

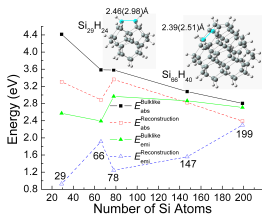
TD-DFT for 100+ atoms



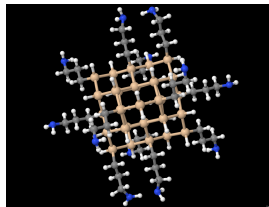
Excited state relaxation crucial



Inverse quantum confinement



Si-C termination beneficial



Deutsche
Forschungsgemeinschaft

DFG

FG 490 Molecular Mechanisms
of Retinal Protein Action

SPP 1243 Quantum Transport
at the Molecular Scale

GRK 1570 Electronic properties
of Carbon based Nanostructures



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