**Introduction**

Light emitting silicon nanoclusters (Si NCs) have been studied extensively over recent years after — 1-nm-size Si NCs were discovered to be photoluminescent with intense blue emission [1]. This phenomenon is demonstrated in Figure 1a where directed light beams from number of crystallites are shown. Dependence of the luminescence wavelength on the NC size has also been demonstrated, as shown in Figure 1b [2].

We have investigated number of different Si NCs and also short oligosilanes and their optical properties and compared different computational methods and experiments. We also suggest new kind of silane modified clusters which have strong optical response as possible light emitters.

**Computational methods**

Molecular structures of the silicon clusters were optimized using density functional theory (DFT) and the BP functional. Time-dependent DFT (TD-DFT) with local density approximation (SVWN), gradient corrected functionals (BP, BLYP, and PBE) and hybrid functionals (B3LYP and PBE0) were employed to obtain excitation energies and the oscillator strengths. Resolution of the identity (RI) approximation, or density fitting, for the Coulomb correction in the hybrid functionals (B3LYP and PBE0) was employed to speed up the computations. For largest clusters also multipole-accelerated RI (MARIJ) was used.

Additionally, second-order approximate coupled cluster model with RI (RI-CC2) was used for short oligosilanes for benchmarking purposes. Computations have been done using TURBOMOLE program package [3].

**Results**

**Surface dimer model**

Surface dimer model suggested by Allen et al. has been often used to explain the luminescence from Si NCs [4]. In this model the dimer has a double well potential in the excited state and the observed blue emission would take place from the outer well in the excited state. To study the validity of this model, potential energy surfaces (PESs) of a single dimer for the ground state and few lowest excited states were investigated. PESs are shown in Figure 2. However, no double well potential is observed. Therefore, to use this model to explain luminescence from Si NCs is questionable.

**Tₙₜ symmetric nanoclusters**

The dependence of the emission wavelength and the cluster size is explained by using the quantum confinement model (QCM), which is also used to explain luminescence in porous silicon [5]. As the size of the NC decreases, the wave function becomes spatially more confined and the energy levels recede from each other. This trend is clearly visible in Figure 3, in which lowest excitation energies for 34 Tₙₜ symmetric clusters (up to Si₂₅H₄₆) were calculated using TD-DFT at MARIJ-BP/def2-SVP level. In our previous work excitation energies and oscillator strengths of various small NCs up to about 1 nm in size have been studied [6, 7, 8, 9]. In all Si NCs the oscillator strengths at the visible region are far too small as compared to the experimentally derived oscillator strength of the emission which is 0.92 [10].

**Silane modified nanoclusters**

For short silane chains oscillator strengths have been observed to increase with the chain length [11]. Therefore, the oscillator strengths of Si NCs could be affected by modifying the NCs surface by attaching silane chains on it. This approach was tried with three different types of clusters [12] these structures are shown in Figure 6.

**Oligosilanes**

Comparison of computational methods and experimental results was possible using oligosilanes (Si₉H₂₉ + m = 1...7) for which accurate and well defined experimental results are available. Both density functional methods and coupled cluster methods were used to obtain optical excitation energies and oscillator strengths [11].

The most accurate RI-CC2 results are presented in Figure 7 with experimental values. Excitation strengths in the visible region by 0.3-0.4 eV. Close to basis set limit (aug-cc-pVQZ) LDA/GGA functionals underestimate the optical gap by 0.7-1.0 eV and hybrid functionals by 0.3-0.4 eV. With smaller basis sets deviations are less, e.g. def2-SVP by ±0.2 eV and def2-TZVP by ±0.2-0.3 eV. These results can be used to estimate the accuracy of computations with larger Si NCs.

**Conclusions**

The computed excited state PESs do not support the surface dimer model which is often used to explain luminescence from Si NCs. The oscillator strengths for Tₙₜ symmetric hydrogen terminated Si NCs are significantly lower than experimentally observed values derived from the luminescence spectrum. In silane capped and bridged clusters both the oscillator strengths and excitation thresholds are comparable to experimental values and these results suggest a possible mechanism for bright luminescence. For accurate optical gaps RI-CC2 method combined with large basis sets is needed but TD-DFT with moderate basis sets can be also used due to cancellation of errors.

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**References**