Supporting Information

Single-electron transport through stabilised silicon nanocrystals

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Absorption properties of colloidal Si NC ensemble

We have studied the optical absorption response of a Si NC ensemble by UV-Vis absorption spectroscopy. The background corrected absorption spectrum of the sample was recorded by a double beam spectrophotometer and is shown in Fig. S1.
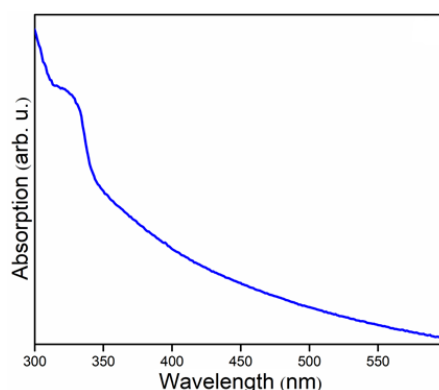

Fig S1 Absorption property of the Si NC ensemble shows a broad maximum; ranging from 316-353 nm.

Fig. S1 shows a broad maximum ranging from 316-355 nm centered at 330 nm. Nature and peak position are the characteristics of the Si NCs. The spectrum is used to get an idea of the wavelength at which it has maximum absorption. But the spectrum is not sufficient to extract the value of the bandgap as the absorption is likely to occur due to transition from the indirect bandgap. However, a rough estimation of Si NCs concentration can be calculated from absorption spectrum by Beer-Lambert law:[1]

$$A = \varepsilon c l \tag{S1}$$

A = measured absorbance, ε = wavelength and size dependent molar absorption coefficient (l mol^{-1} cm^{-1}),[2] c = concentration of the Si NCs, l =optical path length (here 1 cm). From Eq. S1, c is found to be 11.8 µg/l or 0.012 ppm.

Calculation of tunnelling capacitances for Orthodox Theory

In this section, we have calculated tunnelling parameters for Orthodox Theory of DBTJ.[3] The capacitances between tip-Si NC (C_1) and Si NC-Au substrate (C_2) have been calculated by approximating the exact solution between sphere-sphere and sphere-plane capacitances.[4]

Here $C_2 = 4\pi\varepsilon_0 r_{NC} \sin h\alpha \sum_{n=1}^{\infty} \frac{1}{sinh(n\alpha)}$ $\qquad$ S2

The solution is an infinite series and the range *10 < n < 20* will be sufficient to suffice the present condition.[4] Here $\alpha = \ln\left(\frac{S}{r_{NC}} + \sqrt{\frac{S^2}{r_{NC}^2} + \frac{2S}{r_{NC}}} + 1\right)$ and *S* is the distance of separation between the Si NC and the substrate. For *S < r_{NC}* Eq. S2 is converted to,

$C_2 \sim 2\pi\varepsilon_0 r_{NC} \left[\ln\left(\frac{S}{r_{NC}}\right) + \ln 2 + \frac{23}{20}\right]$ $\qquad$ S3

The approximate solution of sphere-sphere capacitance, C_1, can be written in terms of C_2 with a correction factor ß, as follows:

$$C_1\left(r_{\text{tip}}, r_{\text{NC}}, S\right) = ß C_2\left(r_{\text{NC}}, ßS\right) \qquad \text{S4}$$

r_{tip} is the apex radius of the tip and $ß = \dfrac{1}{\left\{1 + \left(\dfrac{r_{NC}}{r_{tip}}\right)\right\}}$

Values of C_1 and C_2 are quite similar as ß values are close to unity (ranging from 0.97 to 0.95 with increasing size) due to $r_{\text{tip}} \gg r_{\text{NC}}$. The capacitance of the NC has been calculated by considering spherical capacitance of any dielectric material i.e. $C_{NC} = 4\pi\varepsilon_{NC}r_{NC}$.

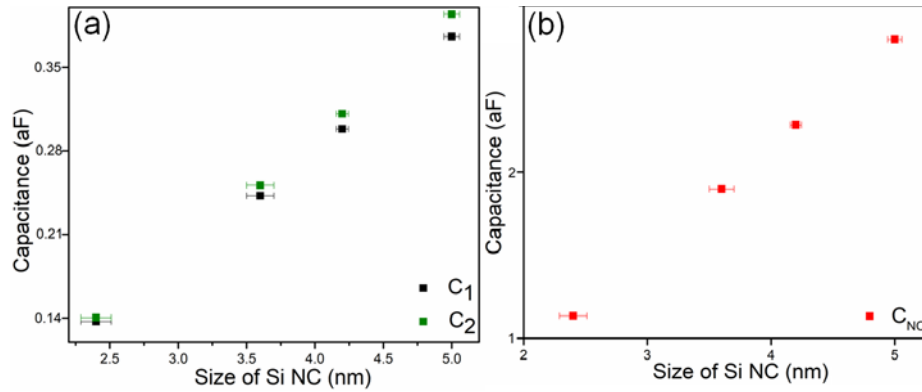**Fig S2** (a) Capacitances of two junctions C_1, C_2 and (b) capacitance of Si NC (C_{NC}). The horizontal bars are the measurement uncertainty of Si NCs during the experiment.

Fig. S2a and S2b show the calculated values of C_1, C_2, C_{NC} with different NC size employing the above equations. As expected the capacitance of Si NC has an increasing trend with the diameter, from 1.14 aF to 2.8 aF, whereas C_1 and C_2 have the same trend with less than one order of magnitude.

References:

1. A. Beer, Ann. Phys., 1852, **162**, 78-88.
2. C. M. Hessel, D. Reid, M. G. Panthani, M. R. Rasch, B. W. Goodfellow, J. W. Wei, H. Fujii, V. Akhavan and B. A. Korgel, Chem. Mater., 2012, **24**, 393-401.
3. A. E. Hanna and M. Tinkham, Phys. Rev. B Condens. Matter., 1991, **44**, 5919-5922.
4. D. Sarid, *Exploring Scanning Probe Microscopy with MATHEMATICA*, Wiley-VCH Verlag GmbH & Co. KGaA, Germany, 2nd Ed., 2007.