# Electronic Supplementary Information

Photoluminescence from FRET Pairs Coupled with
Mie-Resonant Silicon Nanosphere

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1. Absorption and PL Spectra of Ethanol Solutions of FITC and RITC
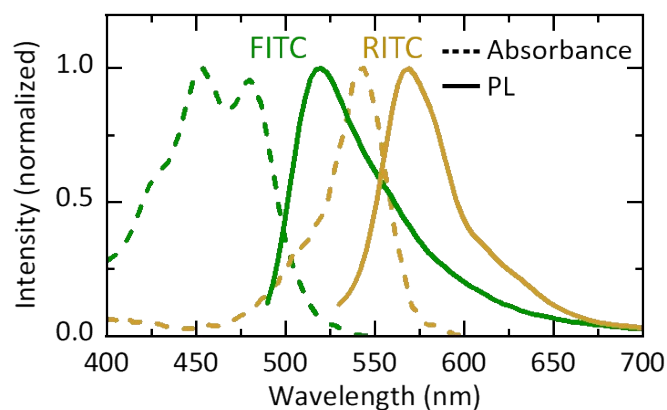

Figure S1. Normalized absorption (dashed curves) and photoluminescence (PL) (solid curves) spectra of ethanol solutions of FITC (green curves) and RITC (yellow curves).

2. Radiative and Nonradiative Rate Enhancement Factors and Antenna Efficiency of a Dipole Placed near a Si NS as a Function of Distance from Si NS Surface
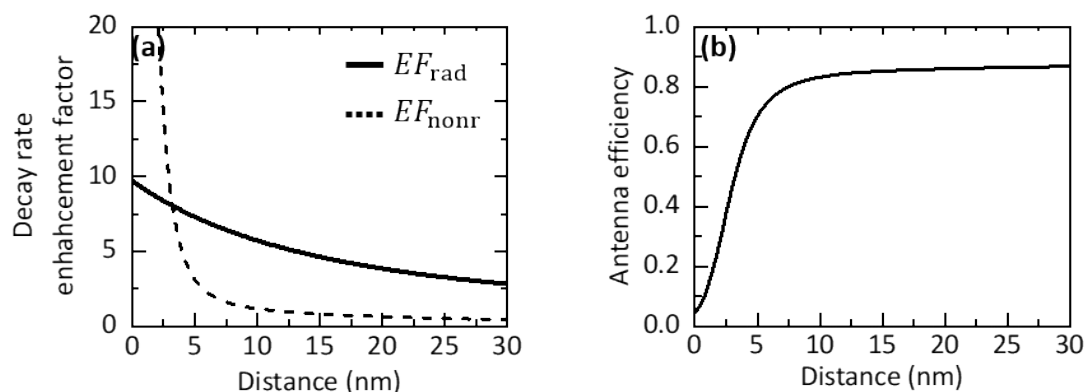
Figure S2. (a) Calculated radiative (EF_{rad}) (solid curve) and nonradiative (EF_{nonr}) (dashed curve) rate enhancement factors and (b) antenna efficiency of a dipole emitter near a Si NS (d_{Si} =120 nm) as a function of the distance from Si NS surfaceat the MD resonance wavelength (522 nm).

3. Size Distribution of Si NSs
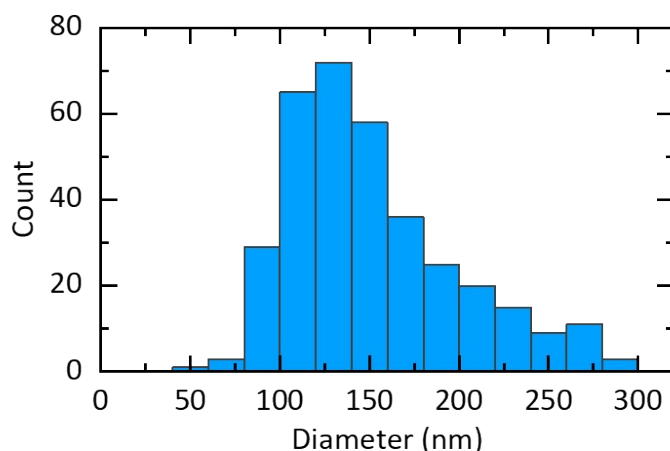
**Figure S3.** Size distribution of Si NSs obtained from TEM images.

4. Estimation of Number of Dye Molecules (FITC and RITC) on Si NS Surface

We estimated the density of FITC (D_{FITC}) and RITC (D_{RITC}) on Si NS surface from the absorption measurements. The procedure is as follows.

First, we measure the absorption spectra of ethanol solutions in which different concentrations of FITC and RITC are dissolved. The data are shown in Figure S4a and S4b, respectively. From these data, the relation between the peak absorbance (at 497 nm in FITC and at 548 nm in RITC) and the concentration is obtained (Figure S4c).

In order to measure absorption spectra of FITC and RITC in Si@FITC and Si@(FITC, RITC) suspensions without being affected by scattering from Si NSs, we etched out Si NSs with NaOH (see photos of Si@(FITC, RITC) suspensions before and after NaOH etching in Figure S4d)[1]. Figure S4e shows the absorption spectra after etching. In Si@FITC, the FITC concentration is estimated from the absorbance at 497 nm. In Si@(FITC, RITC), the RITC concentration in a mixed solution can be estimated from the 548 nm absorbance, since FITC does not have absorption at 548 nm. On the other hand, since RITC has absorption at the absorption maximum of FITC (497 nm), FITC concentration cannot be determined from the 497 nm absorbance. Therefore, we subtract the contribution of RITC to the 497 nm absorbance by using the ratio of RITC absorbance at 497 nm to that at 548 nm. The ratio is 0.25 (see the inset of Figure S4e). Once the contribution of RITC is subtracted, FITC concentration is determined from the 497 nm absorbance by using the data in Figure S4c.

The estimated FITC and RITC concentrations are 9.20 μM and 1.07 μM, respectively, in Si@(FITC, RITC) suspension, and the FITC concentration to 10.7 μM in Si@FITC suspension. These concentrations can be converted to the number of FITC (N_{FITC}) and RITC (N_{RITC}), i.e., N_{FITC} = 5.50 × 10^{15} and N_{RITC} = 0.65 × 10^{15} molecules/mL in Si@(FITC, RITC) suspension, and N_{FITC} = 6.46 × 10^{15} molecules/mL in Si@FITC suspension. Finally, we obtained D_{FITC} and D_{RITC} by dividing these numbers by the total surface area (S_{total}), which was estimated to be 3.11 × 10^{16} nm^2 from the total weight of Si NSs (2.2 mg in 1 mL colloidal solution) and the size distribution of Si NSs in Figure S3. The final values are D_{FITC} = 17.7 and D_{RITC} = 2.08 molecules/100 nm^2 in Si@(FITC, RITC), and D_{FITC} = 20.8 molecules/100 nm^2 in Si@FITC.
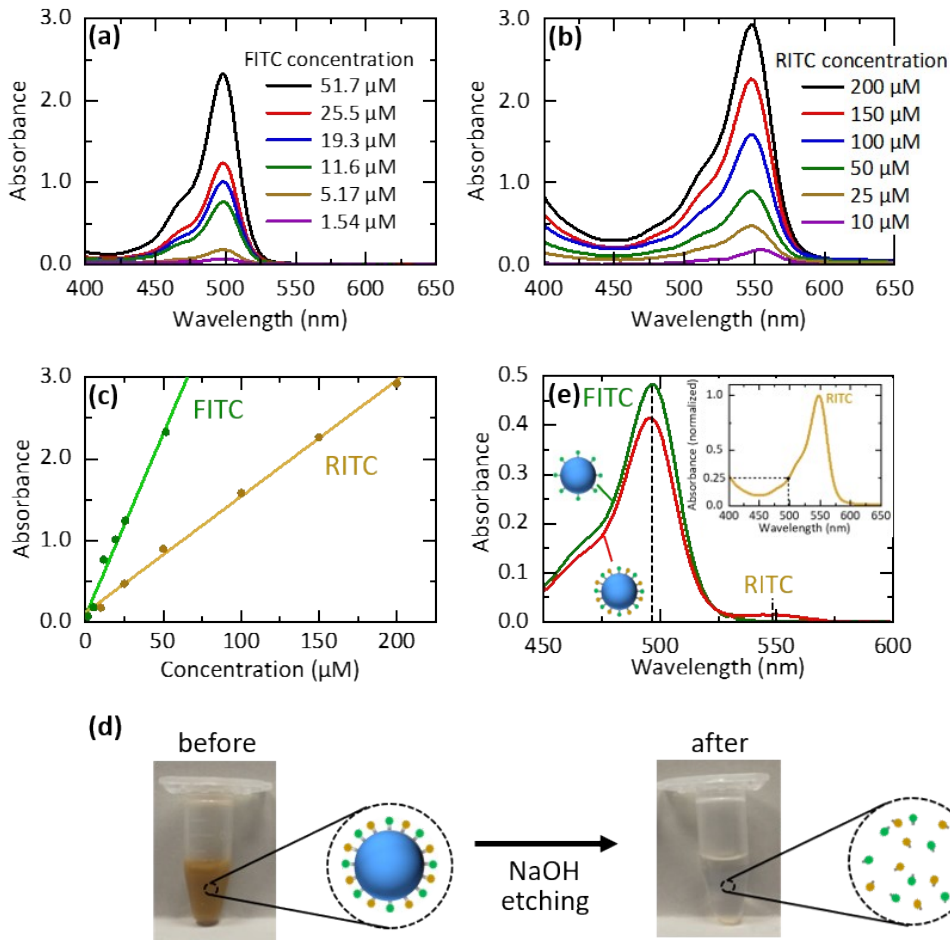
Figure S4. a,b) Absorption spectra of ethanol solutions of a) FITC and b) RITC.c) Peak absorbance of FITC (497 nm) (green dots) and RITC (548 nm) (yellow dots) as a function of the concentration. Solid lines are the results of linear fitting. d) Photographs of Si@(FITC, RITC) suspensions before and after NaOH etching. e) Absorption spectra of Si@(FITC, RITC) (red curve) and Si@FITC (green curve) suspensions after etching. Inset shows normalized absorption spectra of ethanol solutions of RITC. The ratio of absorbance at 497 nm to that at 548 nm is 0.25.

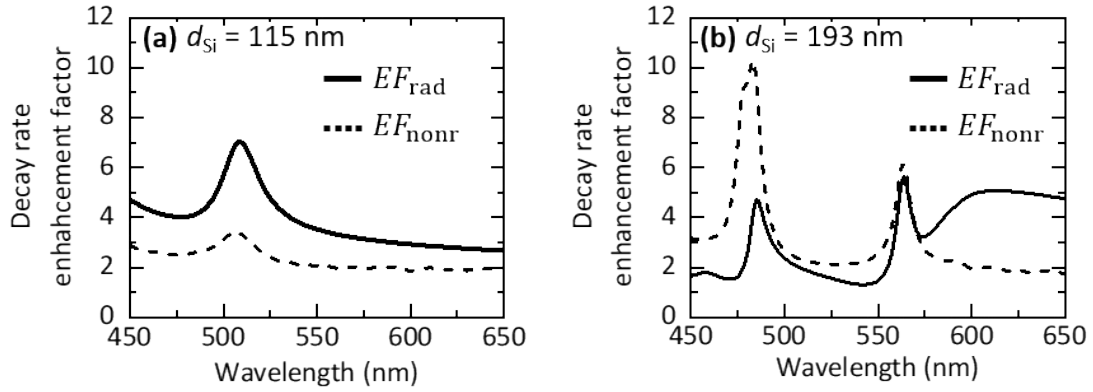### 5. Calculation of PL Decay Rate and Intensity Enhancement Factors for Si@FITC

We calculated radiative (EF_{rad}) and nonradiative (EF_{nonr}) rate enhancement factors of a dipole placed 5 nm from the surface of a Si NS by the method shown in Ref. [2,3]. Figure S5a and S5b show the results obtained for d_{Si} =115 and 193 nm, respectively. By using these data, the decay rate enhancement factor can be calculated as[4],

$$EF_{decay} = \frac{\Gamma_{rad} + \Gamma_{nonr}}{\Gamma_{rad}^0 + \Gamma_{nonr}^0}$$

$$= \frac{\Gamma_{rad}^0 \int f_0 \cdot EF_{rad} d\lambda + (\Gamma_{rad}^0 \int f_0 \cdot EF_{nonr} d\lambda + \Gamma_{nonr}^0)}{\Gamma_{rad}^0 + \Gamma_{nonr}^0}$$

$$= \frac{\int f_0 \cdot EF_{rad}d\lambda + \cdot \int f_0 \cdot EF_{nonr}d\lambda + \dfrac{1 - QY_0}{QY_0}}{1 + \dfrac{1 - QY_0}{QY_0}} \quad , \quad (1)$$

where QY_0 and f_0 are the intrinsic quantum yield of the emitter and the integral-normalized PL spectrum. Under the assumption that $QY_0 = 0.92$ for FITC, EF_{decay} is calculated to be 6.3 for $d_{Si} =$ 115 nm and 4.9 for $d_{Si} =$ 193 nm.

Figure S5. Calculated radiative (EF_{rad}) (solid curves) and nonradiative (EF_{nonr}) (dashed curves) rate enhancement factors for an electric dipole placed 5nm from the surface of a Si NS with $d_{Si} =$ (a) 115 nm and (b) 193 nm.

The PL enhancement factor (EF_{PL}) of a quantum emitter in the vicinity of a nanoantenna can be calculated as[2–5].

$$EF_{PL} = EF_{exc} \cdot EF_{emi} \quad , \quad (2)$$

$$EF_{emi} = \frac{1}{QY_0} \cdot \frac{EF_{rad}}{\int f_0 \cdot EF_{rad}d\lambda + \int f_0 \cdot EF_{nonr}d\lambda + \dfrac{1 - QY_0}{QY_0}} \quad , \quad (3)$$

where EF_{exc} is an excitation enhancement factor, and EF_{emi} is the emission efficiency enhancement factor. EF_{exc} is obtained by averaging the electric field intensity at 5 nm from the surface of a NS. The calculated values are 3.04 for $d_{Si} =$ 115 nm and 2.34 for $d_{Si} =$ 193 nm under 488 nm plane wave excitation. EF_{emi} is calculated by using Figure S5. The final results (EF_{PL}) for $d_{Si} =$ 115 nm and 193 nm are shown in Figure 3c and 3f, respectively, in the main text.

6. Effect of SiO$_2$ Substrate on PL Enhancement Factor Spectra

In calculation of PL enhancement factor spectra (EF_{PL}) in Figure 3 in the main text, we do not consider a SiO$_2$ substrate. Here, we examine the effect of a SiO$_2$ substrate on the spectra. Figure S6 shows the normalized radiative rate enhancement factor spectra for an electric dipole near a Si NS in the presence (red curves) and absence (blue curves) of a SiO$_2$ substrate calculated using FDTD method. Three different dipole positions are considered. We can see that the ED mode is more affected by the substrate than the MD mode. This may suggest that the discrepancy between the experimental and calculated enhancement factor spectra around the ED mode in Figure 3f in the main text is partly due to the existence of a SiO$_2$ substrate in the experiment.
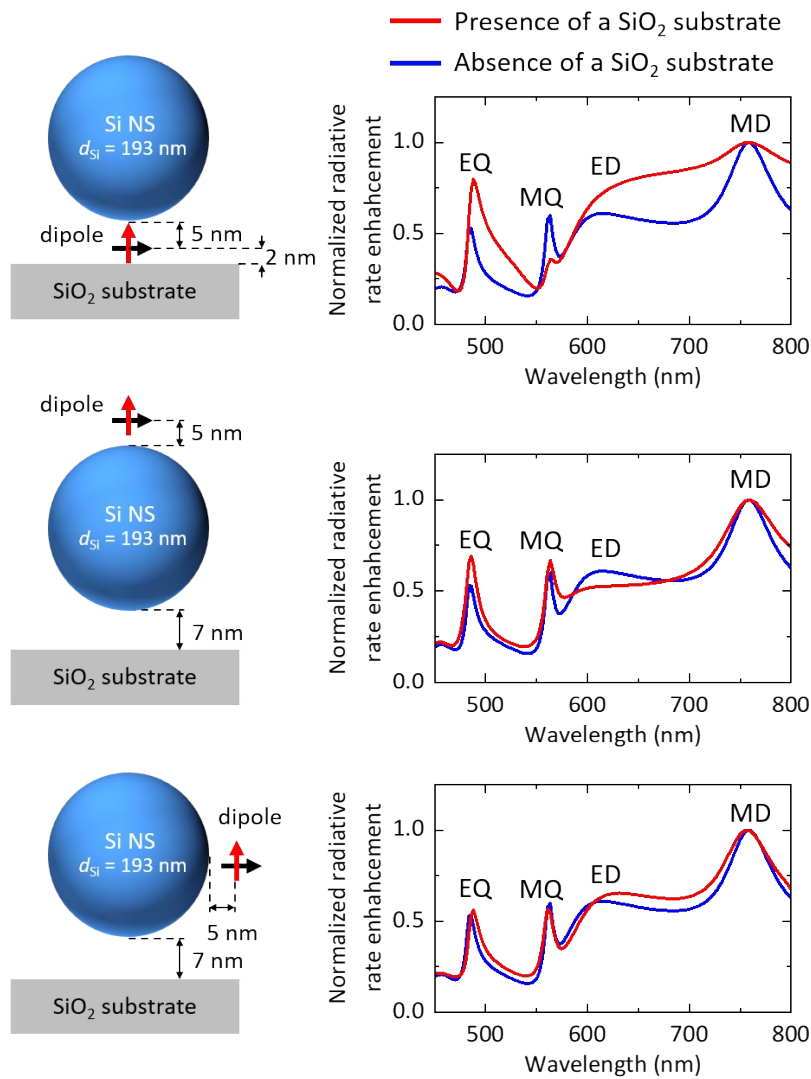

Figure S6. Calculated radiative rate enhancement factor spectra for an electric dipole placed 5 nm from the surface of a Si NS with d_{Si} = 193 nm in the presence (red curves) and absence (blue curves) of a SiO$_2$ substrate.

**7. Scattering and PL Spectra of Si@(FITC, RITC) with Different Si NS Diameters**
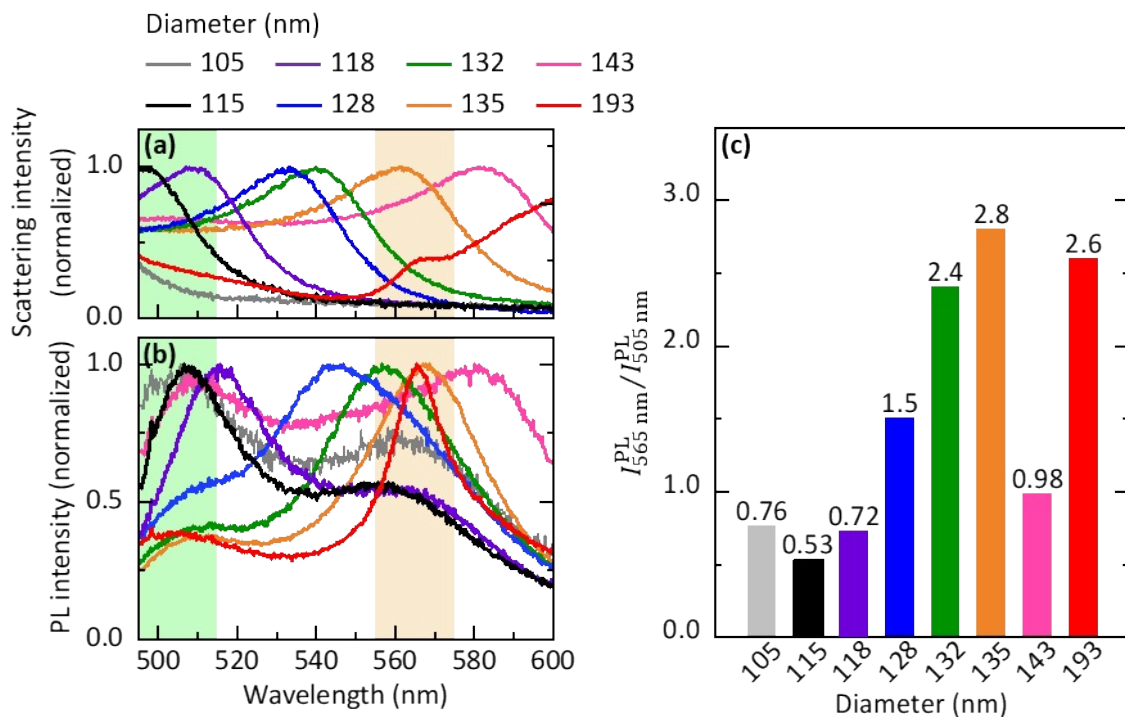
Figure S7. a) Scattering and b) PL spectra of single Si@(FITC, RITC) with d_{Si} = 105 nm to 193 nm. The scattering spectra are normalized at the maximum of the MD mode for d_{Si} = 105 nm to 193 nm, and the PL spectra are normalized at the maximum for all the data. The green and yellow regions represent the PL wavelength of the donor (FITC) and acceptor (RITC), respectively. c) The ratio of the PL intensity at 505 nm (FITC PL peak) and at 565 nm (RITC PL peak).

8. Distributions of $\left|E_D^{Si}\right|$ and $\left|E_D\right|$ at MD Resonance of Si NS
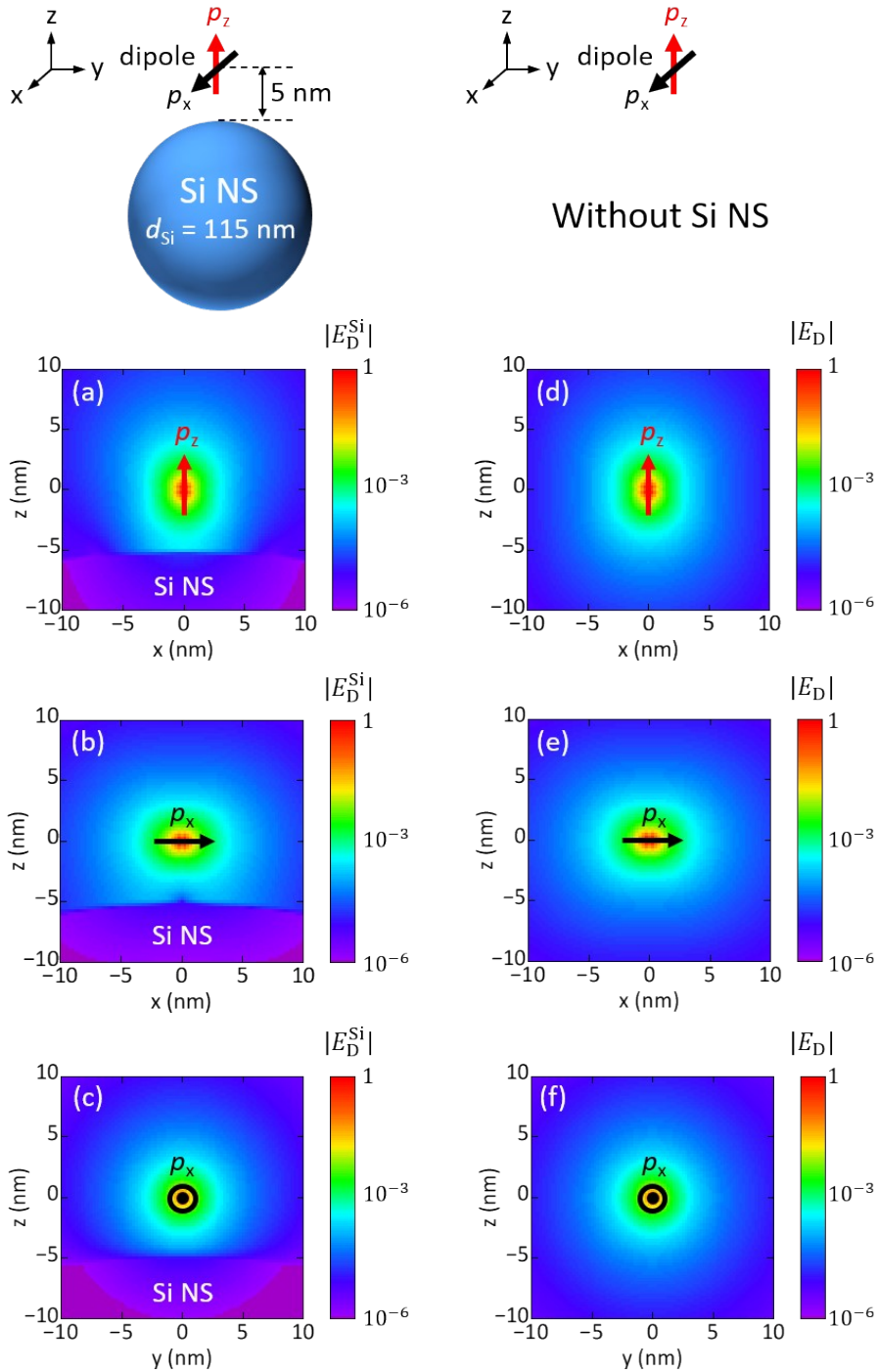
Figure S8. Electric field amplitude produced by an electric dipole source (a-c) with ($\left|E_D^{Si}\right|$) and (d-f) without ($\left|E_D\right|$) a Si NS (d_{Si} = 115 nm) at the MD resonance (wavelength of 508 nm). The dipole source is placed 5 nm from the surface of a Si NS. The orientation of the dipole is along the (a, d) z-axis (p_z) and (b, c, d, f) x-axis (p_x). The color plot is displayed on a logarithmic scale.

9. Distributions of $\left|E_D^{Si}\right|^2/\left|E_D\right|^2$ at ED, MQ and EQ Resonances of Si NS
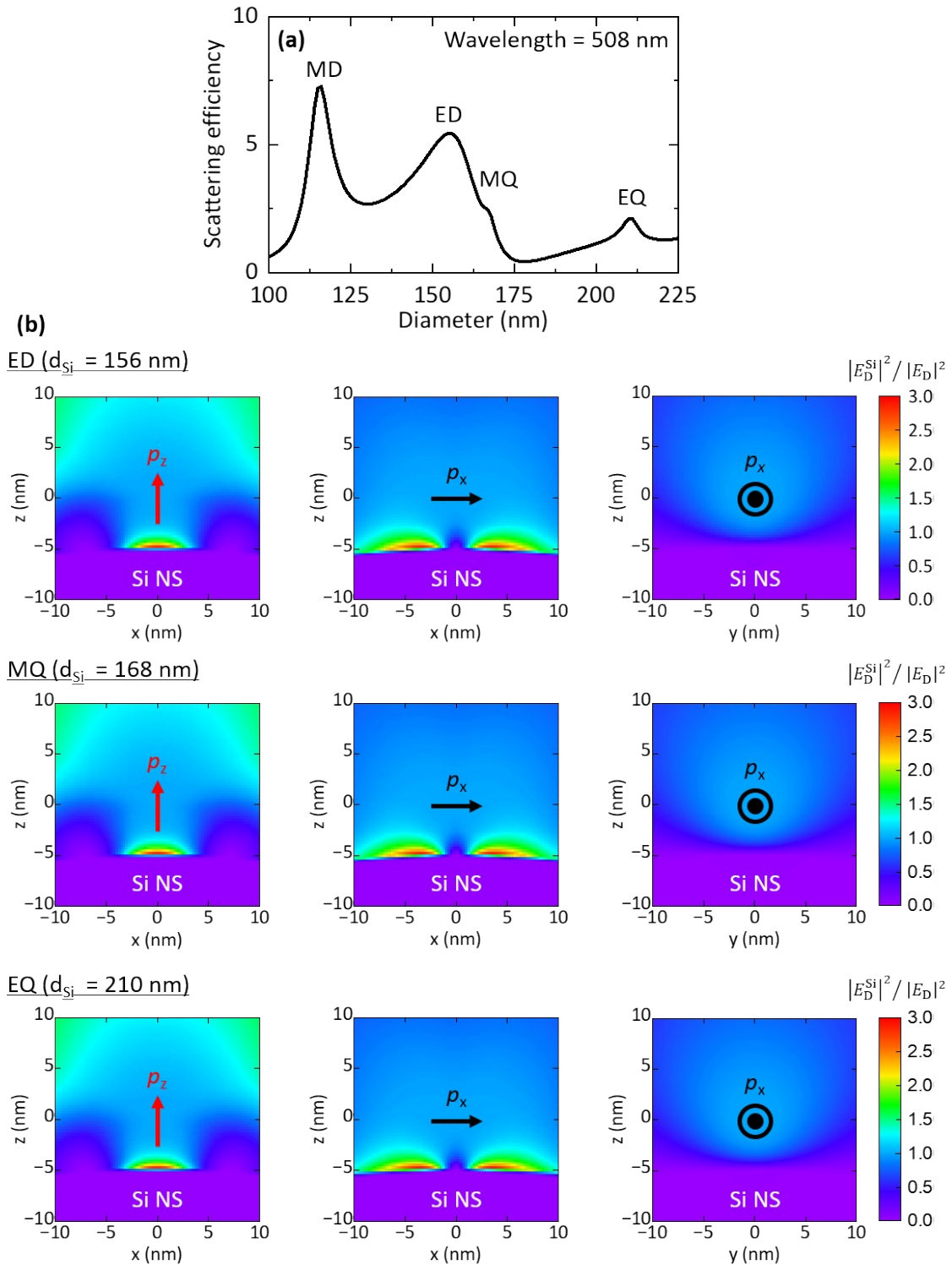
Figure S9. a) Calculated scattering efficiency of a Si NS at the wavelength of 508 nm. The abscissa is the diameter. b) Calculated $\left|E_D^{Si}\right|^2/\left|E_D\right|^2$ at the ED (d_{Si} = 156 nm), MQ (d_{Si} = 168 nm) and EQ (d_{Si} = 210 nm) resonances (wavelength of 508 nm). The dipole source is placed 5 nm from the surface of a Si NS. The orientation of the dipole is along the z-axis (p_z) and the x-axis (p_x).

10. Distributions of $\left|E_D^{Si}\right|^2/\left|E_D\right|^2$ at MD Resonance of Si NS; Dipole-Position Dependence
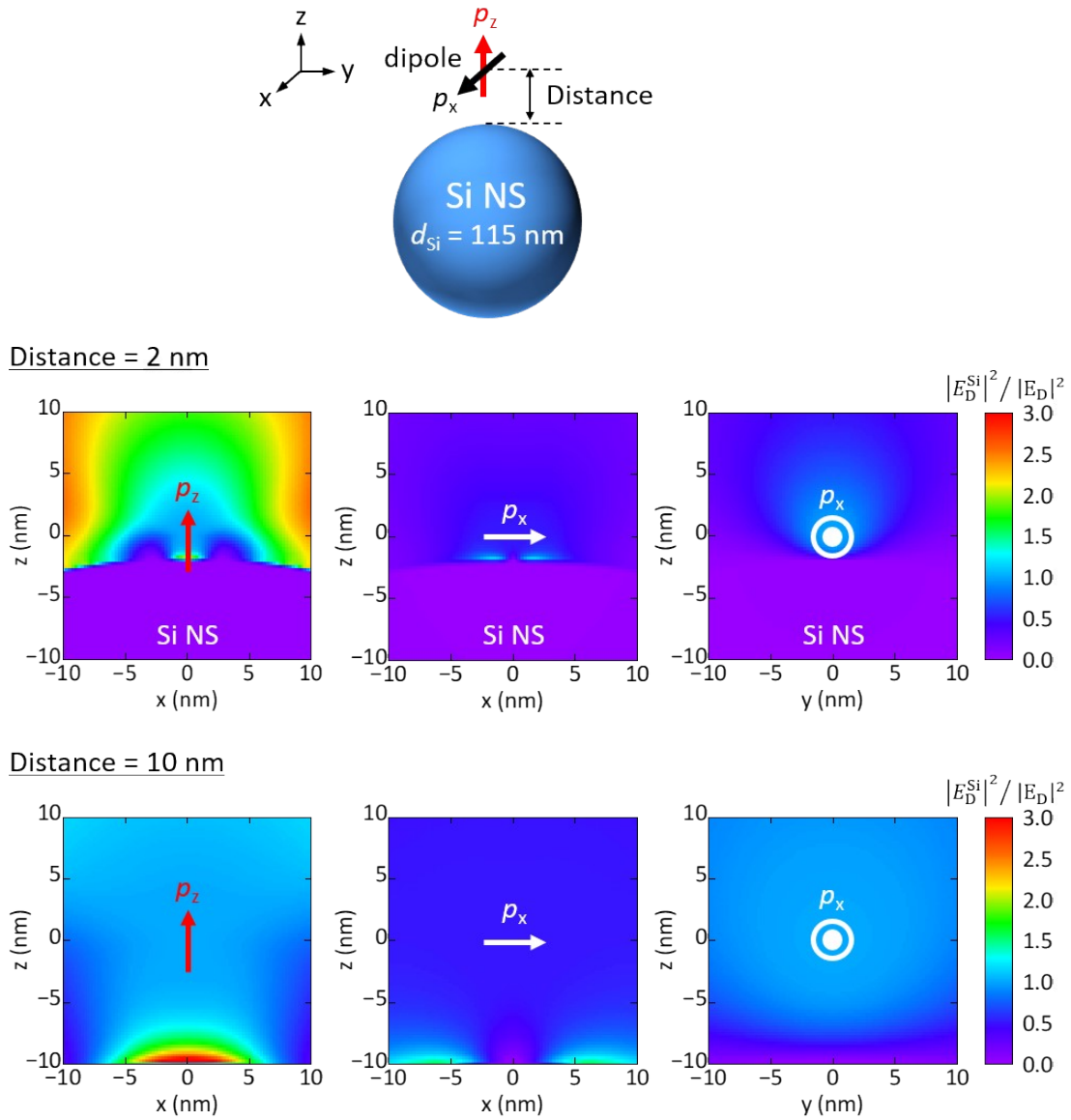
Figure S10. Calculated $\left|E_D^{Si}\right|^2/\left|E_D\right|^2$ at the MD resonance (wavelength of 508 nm) of a Si NS (d_{Si} = 115 nm). The dipole source is placed 2 nm and 10 nm from the surface of a Si NS. The orientation of the dipole is along the z-axis (p_z) and the x-axis (p_x).

Notes and References

1   A. Dhir and A. Datta, *J. Phys. Chem. C*, 2016, **120**, 20125–20131.
2   R. Ruppin, *J. Chem. Phys.*, 1982, **76**, 1681–1684.
3   M. K. Schmidt, R. Esteban, J. J. Sáenz, I. Suárez-Lacalle, S. Mackowski and J. Aizpurua, *Opt. Express*, 2012, **20**, 18609.
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