

All-Dielectric Silicon Nanogap Antennas To Enhance the Fluorescence of Single Molecules

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Supporting Information

ABSTRACT: Plasmonic antennas have a profound impact on nanophotonics as they provide efficient means to manipulate light and enhance light—matter interactions at the nanoscale. However, the large absorption losses found in metals can severely limit the plasmonic applications in the visible spectral range. Here, we demonstrate the effectiveness of an alternative approach using all-dielectric nanoantennas based on silicon dimers to enhance the fluorescence detection of single molecules. The silicon antenna design is optimized to confine the near-field intensity in the 20 nm nanogap and reach a 270-fold fluorescence enhancement in a nanoscale volume of $\lambda^3/1800$ with dielectric materials only. Our conclusions



are assessed by combining polarization resolved optical spectroscopy of individual antennas, scanning electron microscopy, numerical simulations, fluorescence lifetime measurements, fluorescence burst analysis, and fluorescence correlation spectroscopy. This work demonstrates that all-silicon nanoantennas are a valid alternative to plasmonic devices for enhanced single molecule fluorescence sensing, with the additional key advantages of reduced nonradiative quenching, negligible heat generation, cost-efficiency, and complementary metal–oxide–semiconductor (CMOS) compatibility.

KEYWORDS: All-dielectric nanophotonics, silicon resonators, optical antenna, fluorescence enhancement, Mie scattering

Plasmonic metal nanostructures acting as optical antennas provide efficient means to overcome the diffraction limit and localize electromagnetic energy into nanoscale spatial dimensions.¹⁻³ These optical antennas also drastically enhance the interactions between a single quantum emitter and its surrounding photonic environment,⁴⁻⁷ leading to a giant luminescence enhancement,⁸⁻¹⁴ ultrafast emission in the picosecond range,¹⁵⁻¹⁸ and directional emission control.¹⁹⁻²² All of these features make optical antennas ideally suited for the ultrasensitive biodetection of single molecules, especially at the high micromolar concentrations required to meet the biologically relevant physiological conditions.²³⁻²⁵ However, energy transfer to the free electron gas in the metal generates losses, which can lead to severe quenching of the fluorescence emission.^{5,26–28} Additionally, interband transitions in the metal induce absorption at the laser frequency and Joule heating of the antenna and its environment.^{29'} This brings further limitations for the potential applications which require either temperature control (such as biosensing) and high excitation powers (such as nonlinear spectroscopies).

To circumvent the losses involved with plasmonic metal antennas, the use of dielectric nanoparticles, such as silicon or germanium, has recently attracted a keen interest.³⁰⁻³² As compared to gold and silver, these dielectric materials feature weaker absorption coefficients in the visible and the nearinfrared.³³ Like their metal counterparts, subwavelength dielectric particles support spectral resonances, commonly named Mie resonances, which can enhance the local near-field intensity.^{34–39} This approach is conceptually different from dielectric microcavities^{40,41} such as dielectric photonic crystal cavities^{42,43} or planar concentrators^{44,45} that feature high quality Q-factors. On the contrary, subwavelength-sized dielectric particles compensate the low Q-factor of their low order modes by small mode volumes.⁴⁶ Moreover, while spherical metal nanoparticles feature only electric modes, high refractive index dielectric nanoparticles have both electric and

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Figure 1. Silicon nanogap antenna to enhance single molecule fluorescence. (a) Principle of the experiment: a silicon dimer antenna confines light in the nanoscale gap volume and enhances the fluorescence of single molecules diffusing in solution. (b) Scanning electron microscope image of a silicon dimer of 170 nm diameter and 20 nm gap. The silicon thickness is 60 nm. (c,d) FDTD simulations of the electric field intensity distribution enhancement in the plane located at the center height of the silicon dimer. The antenna is illuminated at $\lambda = 633$ nm in normal incidence from the glass substrate with a linear electric field polarized parallel (c) or perpendicular (d) to the dimer axis. Experimental (e) and simulated (f) spectra of the scattering cross-section of the silicon dimer illuminated with an electric field polarized parallel (black line) or perpendicular (red line) to the dimer axis.

magnetic modes that can be of similar strengths.^{31,32,47-49} The presence of both electric and magnetic modes offers novel opportunities to tailor the light scattering⁵⁰⁻⁵⁵ or the chirality of light emission, ⁵⁶ enhance the radiative decay rate constants of nearby emitters, 35,36,57,58 improve the directivity of dielectric optical antennas, ^{59–62} and enhance the Raman scattering process.^{63,64} These features open bright perspectives for alldielectric optical nanoantennas to enhance the fluorescence biosensing of single molecules. Recently, silicon nanogap antennas have been reported to enhance the fluorescence of a dense layer of dyes covering the nanoantennas.⁶³ However, photobleaching effects and the large molecular surface coverage density challenge the quantification of the fluorescence enhancement. Single molecule experiments on the other hand could permit a clear comparison between experimental results and numerical simulations, as well as bringing understanding on the physical origin of the fluorescence enhancement on alldielectric nanoantennas.

Here we use silicon dimer antennas to enhance the fluorescence emission of single molecules diffusing in solutions of micromolar concentration (Figure 1a). Fluorescence correlation spectroscopy (FCS) is implemented to analyze the fluctuations on the fluorescence signal and quantify the average fluorescence brightness per emitter and the size of the detection volume.^{10,13,65} For a dimer of 170 nm silicon nanoparticles with a 20 nm gap, we achieve fluorescence enhancement factors above 200-fold and isolate detection volumes down to 140 \times 10⁻²¹ L, equivalent to $\lambda^3/1800$, or a 3600-fold reduction below the classical 0.5 μ m³ diffraction limited confocal volume. The excitation polarization dependence, the gap size influence, the microsecond transit time, and the excellent agreement with numerical simulations confirm that the fluorescence signal stems from the electromagnetic hot spot in the nanogap of the silicon dimer. This work

demonstrates that all-silicon nanoantennas are a valid alternative to plasmonic devices for enhanced fluorescence sensing, with a sensitivity down to the single molecule level.

The silicon nanoantennas are fabricated with electron beam lithography and reactive ion etching on a thin amorphous silicon film (see Methods section and Supporting Information section 1 for complete details). With this technique, a large number of silicon dimers are fabricated on the same sample with controlled gap sizes. Figure 1b shows a typical antenna example with a 20 nm gap size and 170 nm particle diameter. More scanning electron microscopy images are shown in the Supporting Information, Figure S1.

Finite difference time domain (FDTD) simulations reveal the ability of amorphous silicon dimer antennas to confine the electric field energy in their nanogaps. Figure 1c,d displays the field distributions when illuminating the 20 nm gap antenna with an incident electric field polarized parallel or perpendicular to the dimer axis. An electric field intensity enhancement around 21.5× is achieved in the 20 nm gap when the incident polarization is along the dimer axis, with a spatial distribution that is typical of an electric dipolar resonance. As the gap size is increased to 30 nm, the intensity enhancement drops to 12× (Supporting Information, Figure S2). While higher excitation intensity enhancement factors can be achieved with plasmonic gold antennas (Supporting Information, Figure S3), the higher quenching losses with gold can spoil this effect, so that the net fluorescence gain may eventually not be higher with gold antennas than with silicon.³⁶ Importantly for the biosensing applications, this antenna design sets the maximum field enhancement in the gap region between the silicon nanoparticles and not inside the particles like for most Mie resonances.^{32,66} The FDTD calculations also highlight the strong influence of the incident polarization on the field enhancement in the nanogap since a transverse polarization

(Figure 1d) does not yield any significant field enhancement. This polarization dependence and the resonant feature of this silicon dimer antenna are further emphasized by optical spectroscopy (Figure 1e,f), especially in the 550–750 nm spectral range matching the emission of our fluorescent dyes (Supporting Information, Figure S4).

To assess the optical performance of the silicon dimer antennas for single molecule fluorescence enhancement, the antenna sample is covered by a solution containing 1 μ M of crystal violet fluorescent molecules in a water-glycerol 1:1 solution, in a similar fashion as the studies on plasmonic gold nanorods.^{11,12} These conditions ensure that crystal violet molecules are constantly diffusing around the nanoantennas, so that photobleaching is not a limitation here.^{10,20} Fluorescence traces are recorded (Figure 2a,c,e) and collected



Figure 2. Fluorescence bursts from single crystal violet molecules indicate fluorescence enhancement on silicon nanogap antennas. (a,c,e) Fluorescence time traces and (b,d,f) corresponding photon count histograms recorded on individual silicon nanoantennas, with the excitation electric field polarization set parallel (a,b,e,f) or perpendicular (c,d) to the antenna main axis. The data (c,d) shown here for the perpendicular orientation correspond to a 20 nm gap size; similar results were obtained with a 30 nm gap. The experiments are performed with 1 μ M of crystal violet in water–glycerol 1:1 solution with 50 μ W excitation power at 633 nm. The binning time is 20 μ s, and the count rates are back computed to counts per millisecond to ease comparison with ref 12. The black lines in the histograms are fits by exponentially decaying probability distributions.

in a histogram (Figure 2b,d,f). At the 1 μ M concentration, the confocal volume surrounding the antenna contains about 310 crystal violet molecules that create a near-constant fluorescence background. Fluorescence bursts are clearly seen on top of this background, with intensities depending on the excitation polarization and the gap size. This confirms that the intense fluorescence bursts recorded with parallel excitation on the antenna originate from fluorescent molecules crossing the antenna gap region. We checked that no bursts are detected in the absence of fluorescent molecules (Supporting Information Figure S5), indicating a negligible luminescence background from the silicon antenna itself.

The fluorescence enhancement can be derived from the photon count histograms using the approach in refs 11 and 12. In the confocal reference condition using the same 50 μ W excitation power at 633 nm, the peak fluorescence count per crystal violet molecule is estimated to 1.5 counts/ms. The peak fluorescence intensity using the nanoantenna is determined from the difference between the maximum intensities for the parallel and perpendicular orientations to take into account the fluorescence background. This leads to a fluorescence intensity of 400 counts/ms for the 20 nm gap size, which is equivalent to a $400/1.5 = 270 \times$ fluorescence enhancement. When the gap size is increased to 30 nm, the fluorescence intensity and the enhancement factor decrease to 100 counts/ms and 70×, respectively. From the fluorescence correlation spectroscopy analysis that we detail hereafter, we estimate that less than 0.08 crystal violet molecules are present in the 20 nm gap region at a 1 μ M concentration. This low number and the subtraction

Table 1. Fitting Parameters for the FCS Curves on Silicon Nanoantennas (Figure 3b,c)

	excitat	excitation	
silicon nanogap antenna	perpendicular	parallel	
F (counts/ms)	165 ± 1	183 ± 1	
N^*		0.5 ± 0.1	
N ₀	970 ± 50	970 ± 50	
$ au_{\rm d}$ (μ s)	50 ± 5	0.2 ± 0.1	
Q* (counts/ms)		36 ± 5	
Q_0 (counts/ms)	0.17 ± 0.02	0.17 ± 0.02	
detection volume (zL)	$2.7 \pm 0.2 \times 10^5$	140 ± 30	
fluorescence enhancement		210 ± 40	
volume reduction		3600 ± 700	

method to determine the peak intensity rule out the possibility that the estimated count rates originate from more than a single molecule diffusing in the nanogap. Moreover, as we will show while discussing Figure 4, our experimental observations stand in good agreement with FDTD numerical simulations.

To further confirm the fluorescence enhancement and quantify the near-field antenna volume, we switch the fluorescent molecule choice to Alexa Fluor 647 as in our earlier works on gold nanoantennas,^{10,13,65} and we perform a fluorescence correlation spectroscopy (FCS) analysis. FCS computes the temporal correlation of the time-dependent fluorescence signal, which is used to determine the average number of detected molecules, their mean diffusion time to cross the hot spot volume and the fluorescence brightness per emitter. A major difficulty of these experiments is that the enhanced fluorescence signal from the dimer hot spot can be hidden by the fluorescence background from the large number of nonenhanced molecules still present within the diffractionlimited confocal volume. At the working concentration of 6 μ M, typically 1800 molecules are present in the 0.5 fL diffraction-limited confocal volume probed around the silicon dimer antenna. To improve the contrast between the hot spot enhanced signal and the fluorescence background, we take advantage of two features. First, emitters with low quantum yield exhibit much higher fluorescence enhancement than emitters with high quantum yield (Supporting Information, Figure S6), as their low quantum yield allows a larger benefit to be obtained from the antenna.^{8,10,11,13,14} Therefore, as in our previous studies on plasmonic gold antennas,^{10,13,65} we use 200 mM of methyl viologen in the solution to quench the Alexa 647



Figure 3. Fluorescence enhancement and detection volume in silicon nanogap antennas analyzed by fluorescence correlation spectrocopy (FCS). (a) Fluorescence time traces with excitation electric field parallel (red line) and perpendicular (blue line) to the dimer antenna with 20 nm gap. The experiments are performed with a 6 μ M concentration of Alexa Fluor 647 and 200 mM methyl viologen at 10 μ W excitation power with 100 ms binning time. (b,c) FCS correlation functions corresponding to the traces shown in part a. Dots are experimental data, and black lines are numerical fits, which parameters are summarized in Table 1. (d,e) Comparison of the fluorescence enhancement (d) and detection volume (e) measured in the nanogap of silicon nanoantennas and gold nanoantennas of similar gap sizes, with the excitation electric field polarization set parallel to the dimer axis. The data for gold antennas are taken from our earlier work¹⁰ using the same experimental conditions with Alexa Fluor 647 and 200 mM methyl viologen. The gold nanoantennas have a diameter of 80 nm, a gap size of 20 or 30 nm, a thickness of 50 nm, and are surrounded by a 280 × 140 nm² box aperture in a gold film to further suppress the fluorescence background. The error bars are deduced from the extreme values found in a set of different nanoantennas of similar design parameters (8 and 11 antennas, respectively, for 20 and 30 nm gap sizes). (f) Fluorescence brightness per emitter as a function of the excitation power to show fluorescence saturation occurring at powers higher than 15 μ W. For the silicon antennas, the electric field excitation is set parallel to the dimer axis. For the confocal reference, the data is multiplied by 50× to ease viewing on the same graph.

quantum yield from 30% to 8%. Second, for a mixture of emitters with different brightness (enhanced vs nonenhanced), the contribution to the correlation amplitude G scales as the square of the fluorescence brightness for each population. Hence, a large fluorescence enhancement in the hot spot improves the signal-to-background contrast in FCS by a quadratic manner.^{10,67}

Figure 3a-c displays the raw fluorescence intensity time traces and the FCS correlation functions with excitation polarization parallel and perpendicular to the silicon dimer axis. Larger fluorescence intensities and higher correlation amplitudes are clearly observed when the incident electric field is parallel to the dimer axis (see also Supporting Information, Figure S7 for FCS analysis using crystal violet). This further evidences the coupling between the two silicon particles and the generation of an electromagnetic hot spot in the gap region separating the nanoparticles. The FCS analysis detailed in the Methods section quantifies the average number of fluorescent molecules N^* in the antenna hot spot and their brightness Q^* per emitter. From the data in Figure 3b with parallel excitation and a 20 nm gap size, we find $N^* = 0.5$ molecule with brightness $Q^* = 36$ counts/ms. These values should be compared to the confocal reference of N_{conf} = 1800 molecules with brightness $Q_{conf} = 0.17$ counts/ms. The increase in fluorescence brightness per emitter in the nanogap quantifies the antenna fluorescence enhancement as $Q^*/Q_{conf} = 210$. The FCS data also shows that the volume in the silicon nanogap is $N_{\rm conf}/N^* = 3600$ times lower than the diffraction-limited confocal volume. Additionally, the calibrated 6 μ M Alexa 647 concentration allows us to express the number of molecules N^* as the nanogap detection volume of 140 zL (1 zL = 10^{-21} L), which is equivalent to $\lambda^3/1800$. This volume measured by FCS corresponds well to the 25 × 90 × 60 nm³ = 135 zL value expected from the numerical simulations (Figure 1c). In contrast, the perpendicular excitation leads to a nearly flat correlation curve, with N = 970 molecules and brightness Q = 0.17 counts/ms. This evidences the fact that no volume confinement is achieved for an excitation polarization perpendicular to the dimer axis and confirms the nanogap origin of the signal for a parallel excitation polarization.

As for plasmonic antennas, the local intensity enhancement in the nanogap of silicon antennas critically depends on the gap size. We check this property by comparing the optical performance (enhancement factor and nanogap detection volume) for silicon antennas of 20 and 30 nm gap sizes (Figure 3d,e). A clear increase of the fluorescence enhancement and volume reduction is observed as the gap size is reduced and is consistent with the electric field confinement in the gap region. To assess the properties of the silicon dimer antennas, we also compare our results with gold dimer antennas of similar gap sizes (Figure 3d,e) featuring 80 nm diameter gold particles to have a resonance near the 633 nm excitation and 650–690



Figure 4. Photokinetic rate enhancement in silicon nanogap antennas. (a–c) Numerical simulations of the decay rate constants as a function of the emission wavelength for a perfect dipole emitter with parallel orientation located in the dimer center. The gap size is 20 nm in (a) and 30 nm in (b). All rates are normalized to the dipole's radiative rate in free space. (c) Antenna radiative efficiency (ratio of radiative rate to total decay rate) for a perfect dipole emitter with parallel orientation located in the dimer center with 20 nm (red) and 30 nm (orange) gap size. (d) Normalized fluorescence decay traces of Alexa Fluor 647 with 200 mM methyl viologen obtained on a 20 nm gap silicon antenna with excitation light parallel (red) and perpendicular (blue) to the dimer axis. Black lines are numerical fits convoluted by the instrument response function (IRF) which are used to determine the fluorescence lifetimes. (e) Numerical simulations of the fluorescence enhancement factor $\eta_{\rm F}$ using eq 1 as a function of the initial quantum yield of the emitter (in homogeneous environment without the antenna) for silicon antennas with 20 nm (red line) and 30 nm (orange line) gap sizes. The excitation wavelength is 633 nm, and the emission is averaged over the 650–690 nm region for a dipole with parallel orientation to the dimer main axis. The dots represent the experimental data, and CV stands for the experiments on crystal violet and A647 for the measurements on Alexa Fluor 647 with 200 mM methyl viologen. The vertical error bars represent the extreme values found in the set of experiments; the horizontal error bars indicate a 20% uncertainty on the fluorescence quantum yield. The lines represent the evolution predicted using only the numerical simulations results. They are not a fit to the experimental data; there is no free parameter.

nm emission for Alexa 647.¹⁰ The experimental conditions are identical between the experiments so that the fluorescence enhancement factors and detection volumes can be readily compared. Remarkably, the silicon antennas have fluorescence enhancement and optical confinement properties that are very similar to the gold antennas of similar gap sizes. This is a very positive indication for the field of all-dielectric nanophotonics and a further motivation to reach sub-10 nm gaps by improving the challenging lithography and etching of silicon.

The dependence of the brightness per emitter with the excitation power shows a saturation trend that is typical of fluorescence (Figure 3f). This further supports our conclusions and shows that our data is not affected by laser leakage on the detection channel or other spurious effects. Moreover, count rates per molecule above 40 000 counts/s can be readily obtained with the silicon antenna, while the fluorescence brightness saturates to values below 1000 counts/s for the confocal reference in the presence of methyl viologen.

The fluorescence enhancement results from different phenomena: higher local excitation intensity leading to increased excitation rate, increased radiative emission rate for the dipole emitter inside the gap, new nonradiative decay routes opened by energy transfer to the material, and improved collection efficiency as the antenna can beam the fluorescence emission toward the detection numerical aperture. FDTD numerical simulations show that the emission is dominated by the contribution from dipolar sources with orientation parallel to the antenna main axis (Supporting Information, Figure S8) and that the collection efficiency enhancement can be neglected in the case of our silicon dimer antennas (Supporting Information, Figure S9). Therefore, the fluorescence enhancement factor $\eta_{\rm F}$ can be expressed as⁶⁸

$$\eta_{\rm F} = \frac{I_{\rm exc}^*}{I_{\rm exc}} \frac{\Gamma_{\rm rad}^*}{\Gamma_{\rm rad}} \frac{1}{1 - \phi_0 + \phi_0 (\Gamma_{\rm rad}^* + \Gamma_{\rm loss}^*) / \Gamma_{\rm rad}}$$
(1)

where $I_{\text{exc}}^*/I_{\text{exc}}$ is the excitation intensity enhancement in the nanogap, $\Gamma^*_{rad}/\Gamma_{rad}$ is the enhancement of the radiative decay rate constants, $\phi_0 = \Gamma_{\rm rad} / (\Gamma_{\rm rad} + \Gamma_{\rm nr})$ is the intrinsic quantum yield of the fluorescent molecule in homogeneous solution and Γ^*_{loss} is an additional decay rate constant describing the nonradiative energy transfer to the antenna's material induced by ohmic losses. The influences of the antenna on the radiative rate Γ_{rad}^* , the nonradiative rate Γ_{loss}^* , and the total decay rate $\Gamma_{tot}^* = \Gamma_{rad}^* + \Gamma_{loss}^*$ are computed by FDTD and shown in Figure 4a– b for silicon antennas of 20 and 30 nm gap sizes, taking into account the complex permittivity of amorphous silicon.^{33,72} In agreement with the reciprocity theorem, 28 the computed radiative rate enhancement $\Gamma^*_{
m rad}/\Gamma_{
m rad}$ appears very close to the excitation intensity enhancement I_{exc}^*/I_{exc} and increases as the gap size is reduced. However, our calculations reveal a nonnegligible contribution of the nonradiative losses, which decrease the antenna's radiative efficiency in the visible region used to probe the fluorescent dyes (Figure 4c). While amorphous silicon has an almost real permittivity in the nearinfrared minimizing the optical losses,³⁶ the remaining absorption in the visible range is a phenomenon that must be taken into account. Fortunately, for low quantum yield emitters ($\phi_0 < 20\%$), the Purcell enhancement of the radiative rate can compensate the quenching effect of the ohmic losses, leading to a net enhancement of the apparent quantum yield (Supporting Information, Figure S6).

We confirm the simulated decay rate enhancement by recording the fluorescence decay kinetics upon picosecond pulsed excitation. Figure 4d displays typical decay traces for Alexa Fluor 647 with 200 mM methyl viologen on a 20 nm gap silicon antenna. While the decay kinetics are similar for the confocal reference and the antenna with perpendicular orientation (Supporting Information, Figure S10), turning the excitation polarization to parallel induces a clear acceleration of the decay dynamics. While a single exponential model with 350 \pm 15 ps lifetime accounts well for the observed decay dynamics in the case of the antenna with the excitation in perpendicular orientation, we find that a biexponential model is needed to describe the decay in the case of the excitation parallel to the silicon antenna dimer. This biexponential model accounts for the respective contributions of the N^* molecules in the gap region (that we assign to the newly appearing short lifetime contribution) and the N_0 molecules in the confocal volume (away from the antenna, which have a 350 ps lifetime independent of the excitation polarization). Taking into account the convolution with the instrument response function (IRF), our data indicate a fluorescence lifetime of 150 ± 20 ps in the gap region. This lifetime reduction may seem weak as compared to the 40× decay acceleration computed in Figure 4a. It is important to keep in mind here that a significant contribution in the experimentally observed decay dynamics comes from the internal nonradiative rate $\Gamma_{\rm nr} = 0.67 \text{ ns}^{-1}$ of Alexa Fluor 647 and the quenching rate $\Gamma_{\rm q} = 1.9 \text{ ns}^{-1}$ set by methyl viologen.⁶⁵ These contributions must be subtracted to the observed total decay rate to recover only the contribution from the local density of optical states (LDOS which encompasses both radiative Γ^*_{rad} and nonradiative Γ^*_{loss} transitions set by the photonic environment). This provides a decay rate of 0.28 ns^{-1} for the confocal reference and 4.1 ns^{-1} for the 20 nm gap silicon antenna with parallel excitation, leading to an LDOS enhancement of $15 \pm 3 \times$ which clearly demonstrates the significant influence of the silicon antenna on the LDOS. The discrepancy with the predicted values from the numerical simulations stems mainly from the spatial and orientational averaging within the gap region that affects the experimental data, as well as local defects on the fabricated nanodiscs.6

Altogether, the numerical simulations allow the computation of the net fluorescence enhancement $\eta_{\rm F}$ as a function of the intrinsic quantum yield ϕ_0 of the emitter in homogeneous solution following eq 1.⁷⁰ The lines in Figure 4e are predicted by solely using the numerical simulation results; i.e., they are not a fitting to the experimental data. The good agreement with the experimental observations for crystal violet and Alexa Fluor 647 and for both gap sizes further supports our conclusions. Reducing the emitter's intrinsic quantum yield and decreasing the gap size maximize the contributions of the radiative rate and of the excitation intensity enhancement in the silicon nanogap. We clearly observe that enhancements of several hundred are reached and even higher values can be foreseen for further reduced gap sizes. Altogether, these results establish that silicon dimers with nanometer gap sizes work as nanoantennas and enhance the emission from single molecules diffusing across the nanoscale gap region. The fluorescence enhancement in silicon nanogap antennas is thoroughly explained by a combination of excitation intensity and radiative rate enhancement with near similar strengths.

In conclusion, we have experimentally demonstrated fluorescence brightness enhancement up to 270× for single molecules diffusing across the nanogap of silicon dimer antennas. The low Q-factor of the resonance is compensated by the ultralow mode volume of $\lambda^3/1800$ to enhance simultaneously both the excitation intensity and the radiative decay rate by about 20×. The low resonance Q-factor turns out to be an advantage as it accommodates the full emission spectrum of the fluorescent dye at room temperature, avoiding the narrow spectral range of operation and the cryogenic temperatures found with high Q-factor microcavities. Our results show that amorphous silicon is a valuable alternative to plasmonic materials to design optical antennas and use them for single molecule fluorescence sensors. As compared to gold antennas, our silicon antenna design circumvents the major limitations of nonradiative quenching and heat losses in the metal. Moreover, silicon is cost-effective and compatible with CMOS processing. The demonstration that silicon nanogap antennas are efficient platforms to probe single fluorescent molecules constitutes an important step forward for the implementation of molecular sensors with on-chip CMOScompatible nanophotonic devices.

Methods. Nanoantenna Fabrication. Electron beam lithography and reactive ion etching are used to fabricate the nanoantennas on a thin silicon film. Briefly, an amorphous silicon layer is deposited on a 150 μ m thick microscope glass coverslip by plasma assisted reactive magnetron sputtering (Buhler, HELIOS).⁷¹ This method offers an excellent uniformity and accuracy on the 60 nm thickness of the silicon layer. The silicon layer is then covered by a 60 nm thick poly(methyl methacrylate) layer for electron beam lithography and a 15 nm thick nickel layer to create a hard mask for reactive ion etching by lift-off process. The areas unprotected by the nickel mask are etched by a gas mixture containing SF₆, O₂, and CHF₃ to create the dimer antennas (see Supporting Information section 1 for complete details). While high temperature annealing or femtosecond laser heating can induce the crystallization of silicon,⁴⁷ our fabrication procedure does not meet the conditions to induce the phase transition of silicon: our electron-sensitive polymer does not resist to high temperature, and our RIE is performed at 20 °C as the sample is placed onto a table cooled by a water flow. The amorphous nature of the silicon used in our antennas is exemplified by the nice agreement with the numerical simulations using the reference permittivity for amorphous silicon (Figure 4e).

Experimental Setup. Optical spectroscopy on individual scatterers is performed with a homemade confocal microscope. Incident light illumination is obtained by a 250 W Quartz Tungsten Halogen lamp (Oriel QTH). The light coming from the fiber is then polarized using a Glan-Thompson linear polarizer and focused from the top of the sample with a ×10 objective (Olympus) with a numerical aperture of 0.22. The light scattered by the resonator is collected by a ×100 microscope objective, numerical aperture of 0.7, with a long working distance (10 mm) (Mitutoyo). The collected light is then focused with an optical fiber with a core diameter of 62.5 μ m on the spectrometer (isoplane, Princeton Instruments) equipped with a Peltier-cooled CCD detector.

The fluorescence experiments are carried upon an inverted confocal microscope (with 40×, 1.25 NA water-immersion objective from Zeiss) customized with a three-axis piezoelectric stage. Linearly polarized He-Ne laser with 10 μ W incident power is used as an excitation source at 633 nm. For lifetime measurements, the excitation source is a picosecond laser diode operating at 636 nm (Pico-Quant LDH-P-635). The emitted fluorescence is collected in epi-detection mode using a dichroic mirror followed by 670 ± 20 nm bandpass filter and two avalanche photodiodes (PicoQuant MPD-5CTC). A 30 µm pinhole in the detection path rejects the off-focal signal and sets the 0.5 fL confocal detection volume. For fluorescence lifetime measurements, the photodiode output is sent to a fast timecorrelated single photon counting module (PicoQuant PicoHarp 300). Prior to all the experiments, the antennas are rinsed with ethanol and are exposed to UV ozone treatment for 1 min to remove any possible organic impurities.

Fluorescence Correlation Spectroscopy. The temporal fluctuations of the fluorescence intensity F(t) are analyzed with a hardware correlator (Flex02-12D/C correlator.com, Bridgewater NJ) with 12.5 ns minimum channel width to perform fluorescence correlation spectroscopy (FCS). FCS computes the temporal correlation of the fluorescence signal $G(\tau) = \langle F(t).F(t+\tau) \rangle / \langle F(t) \rangle^2$, where τ is the delay (lag) time, and $\langle \rangle$ indicates time averaging. In the silicon dimer experiments, the total fluorescence signal is the sum of the enhanced fluorescence from molecules within the nanogap region and the fluorescence from the molecules still present in the diffraction-limited confocal detection volume. As in our earlier works on plasmonic antennas, ^{10,13,65} the FCS analysis discriminates between these contributions by considering the trace as a sum of two molecular species with different number of molecules and brightness: N* molecules within the dimer gap region with brightness Q^* , and N_0 background molecules with brightness Q₀ diffusing away from the region of interest. An essential feature in FCS is that the molecules contribute to G in proportion to the square of their fluorescence brightness, so that the fluorescence from molecules in the nanogap region experiencing the maximum enhancement will have a major contribution in the FCS correlation. 10,67 The temporal correlation of the fluorescence intensity F can be written as

$$G(\tau) = \frac{\langle F(t) \times F(t+\tau) \rangle}{\langle F(t) \rangle^2}$$

= 1 + $\frac{N^* Q^{2*} G_d^*(\tau) + N_0 Q_0^2 G_{d0}(\tau)}{(N^* Q^* + N_0 Q_0)^2}$ (2)

where $G_d^*(\tau)$ and $G_{d0}(\tau)$ are the normalized correlation functions for each species taken individually based on a classical three-dimensional model:

$$G_{di}(\tau) = \frac{1}{(1 + \tau/\tau_{d,i})\sqrt{1 + s_i^2 \tau/\tau_{d,i}}}$$
(3)

 $\tau_{d,i}$ stands for the mean residence time (set by translational diffusion) and s_i is the ratio of transversal to axial dimensions of the analysis volume, whose value is set to s = 0.2 as it has negligible influence on the estimates of the number of molecules and brightness within the gap (N^*, Q^*) . To extract the number of molecules within the gap (N^*) and the corresponding fluorescence brightness Q^* , we use the asymptotic value of the correlation function toward zero lag time:^{10,13,65}

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$$G(0) = 1 + \frac{N_0 Q_0^2 + N^* Q^{*2}}{(N_0 Q_0 + N^* Q^*)^2}$$
(4)

The value of total fluorescence intensity F (i.e, $N_0Q_0 + N^*Q^*$) is known from the experimental measurement, thus replacing $N^*Q^* = F - N_0Q_0$ into eq 4, we obtain the fluorescence brightness and number of molecules within the nanogap region:

$$Q^* = \frac{F^2(G(0) - 1) - N_0 Q_0^2}{(F - N_0 Q_0)}$$
(5)

$$N^* = \frac{(F - N_0 Q_0)^2}{F^2 (G(0) - 1) - N_0 Q_0^2}$$
(6)

These expressions show that, in addition to the experimentally measured parameters F and G(0), we need to estimate the number of molecules and brightness (N_0, Q_0) for the molecules diffusing away from the nanogap region. The fluorescence brightness Q_0 is set according to the value found for the confocal reference Q_{conf} . The number of background molecules N_0 is deduced from the fluorescence intensity when the excitation polarization is set perpendicular to the dimer axis.

Numerical Simulations. The near-field distributions are calculated with finite-difference time-domain FDTD method (RSoft Fullwave software) with a mesh size of 1 nm. The antenna parameters are set to reproduce the fabricated devices, with a cylindrical shape with 170 nm diameter, 60 nm height, and 20 or 30 nm gap, taking into account a glass substrate (refractive index 1.52) and water superstrate. The excitation wavelength is 633 nm. The permittivity for amorphous silicon is taken from refs 33 and 72. The decay rate constants and emission patterns are performed using an in-house finite difference time domain (FDTD) code.⁷⁰

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.6b02076.

Silicon nanoantenna fabrication, numerical simulation of electric field intensity enhancement in silicon dimer nanoantennas, comparison with electric field intensity enhancement in gold dimer nanoantennas, overlap between the antenna resonance and the fluorescence absorption and emission spectra, luminescence background when no fluorescent dye is present, quantum yield enhancement for 20 nm silicon nanogap antenna, FCS analysis of crystal violet fluorescence traces on silicon antenna, comparison of decay rates for dipolar source parallel and perpendicular to the gap, radiation patterns for a dipolar source parallel and perpendicular to the gap, and reference fluorescence decay kinetics on confocal setup (PDF)

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Notes

The authors declare no competing financial interest.

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Letter

Supporting Information for All-Dielectric Silicon Nanogap Antennas to Enhance the Fluorescence of Single Molecules

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This document contains the following supporting information:

- 1. Silicon nanoantenna fabrication
- 2. Numerical simulation of electric field intensity enhancement in silicon dimer nanoantennas
- 3. Comparison with electric field intensity enhancement in gold dimer nanoantennas
- 4. Overlap between the antenna resonance and the fluorescence absorption and emission spectra
- 5. Luminescence background when no fluorescent dye is present
- 6. Quantum yield enhancement for 20 nm silicon nanogap antenna
- 7. FCS analysis of crystal violet fluorescence traces on silicon antenna
- 8. Comparison of decay rates for dipolar source parallel and perpendicular to the gap
- 9. Radiation patterns for a dipolar source parallel and perpendicular to the gap
- 10. Reference fluorescence decay kinetics on confocal setup

1. Silicon nanoantenna fabrication

The all-silicon nanogap antennas are fabricated by creating a mask with electron beam lithography in a poly(methyl methacrylate) PMMA layer coated on a 60 nm thick silicon layer. The amorphous silicon layer is deposited on a 150 µm thick silica coverslip by Plasma Assisted Reactive Magnetron Sputtering (PARMS) using a Buhler HELIOS machine. The layers are obtained by the sputtering of two silicon targets with a plasma of Argon (30 sccm) excited with a mid frequency source (4500 W at 40 kHz) at low pressure (5.10⁻⁴ mbar). The precise control of the thickness of the deposited layer is carried out using an *in-situ* optical monitoring system. This system measures the evolution of the monochromatic transmission during deposition. The monitoring wavelength is chosen to be equal at 1500 nm. At this wavelength the absorption of silicon layers is negligible and the real part of the refractive index is equal to 3.695. Deposition is stopped by using a trigger point technique, *i.e.* when the transmission of the deposited layer on a fused silica test glass is equal to 46.3%. Precision and uniformity of the thickness is better than 0.5%. After deposition, the samples are cleaned in successive ultrasound baths in acetone and isopropyl alcohol (IPA, propan-2-ol), dried under clean nitrogen flow and exposed to oxygen plasma at 150°C (Nanoplas, France) for 10 minutes. A 60-70 nm thick commercial PMMA positive e-beam resist (ARP-679, Allresist, Germany) diluted at 2% in ethyl lactate solvent is spin-coated at 4000 rpm onto the silicon surface and baked on a hotplate to remove the remaining solvent and harden the PMMA layer. A second conducting polymer layer (SX AR-PC 5000/90.1 from Allresist, Germany) of thickness of 30 nm is spin-coated on the first PMMA ebeam resist to reduce the sample charging and to increase the EBL resolution. The samples are exposed to electron beam using an EBL tool (Pioneer, Raith, Germany) equipped with field emission gun (FEG) electron source (acceleration voltage of 20 kV, apertures of 7.5 and 10 µm, beam current of 18 to 30 pA). We varied both the designed distances between the features and the expose dose in order to finely tune the gap between the particles. The nominal dose is $120 \ \mu\text{C/cm}^2$. Several dose coefficients are tested (0.8, 0.9). For example, the 20 nm nanogap antennas are obtained with a dose coefficient of 0.9 corresponding to a dose of $0.9 \times 120 \,\mu\text{C/cm}^2$. After exposure, the conducting layer is removed in deionised water, and the PMMA is developed in a commercial solution (AR 600-55 from Allresist) during 60 seconds. A 15 nm thick metal nickel mask is then evaporated on the sample under vacuum (Auto 306 tool from Edwards, UK). After metallization, a lift-off process is performed in ethyl lactate using ultrasonic cleaning bath. During the lift-off, the remaining e-beam resist and the excess of nickel are removed. Finally, the sample is rinsed in deionized water and dried under nitrogen flow. The unprotected areas are etched in a RIE tool (MG-200, Plassys, France) by a gas mixture containing SF₆, O₂ and CHF₃ (respective fluxes 20, 8 and 5 sccm) for 10 seconds, alternated with a pure O_2 plasma for 5 seconds. Excited SF₆ is known to efficiently etch silicon and the admixture of CHF₃ gas is used to passivate the vertical feature walls and to etch the silicon oxide on the very reactive silicon surfaces during the process. This process offers a very good etching anisotropy and nearly vertical walls. After RIE, the remaining nickel is removed chemically in the acid solution of HCl and FeCl₃. Finally, the samples are rinsed in deionized water and dried under nitrogen flow. Scanning

electron microscopy images are performed on a FEI DB235 microscope with field emission gun and 5 kV acceleration voltage, providing about 4-5 nm spatial resolution.





Figure S1. (a) SEM image of an array of silicon dimer antennas with gaps measured around 20 nm. b) SEM images of silicon dimers in function of the e-beam exposure dose coefficient allowing to fabricate the 30 nm gap (dose 0.8) and the 20 nm gap antennas (dose 0.9). For higher doses, the antennas are bridged. The scale bar is 100 nm.

а



2. Numerical simulation of electric field intensity enhancement in silicon dimer nanoantennas

Figure S2. FDTD simulations of the electric field intensity distributions around the silicon dimer of 170 nm diameter with 20 nm gap (a,b) and 30 nm gap (c,d). The silicon antenna is illuminated at λ = 633 nm in normal incidence from the glass substrate with a linear electric field polarized parallel to the dimer axis. The images in (a,c) correspond to the horizontal plane crossing the center height of the dimer, while the images (b,d) are vertical cross-sections along the main dimer axis. The color scales are common for (a,c) and (b,d) to ease comparison between the gap sizes.



3. Comparison with electric field intensity enhancement in gold dimer nanoantennas

Figure S3. FDTD simulations of the electric field intensity distributions around the gold antenna of 80 nm diameter particles with 20 nm gap (a,b) and 30 nm gap (c,d). The gold antenna is illuminated at λ = 633 nm in normal incidence from the glass substrate with a linear electric field polarized parallel to the dimer axis. The images in (a,c) correspond to the horizontal plane located inside the antenna at 7 nm from the gold-glass interface, while the images (b,d) are vertical cross-sections along the main dimer axis. The color scales are common for (a,c) and (b,d) to ease comparison between the gap sizes.

4. Overlap between the antenna resonance and the fluorescence absorption and emission spectra



Figure S4. Spectral overlap between the dark-field scattering spectrum for the silicon antenna with 20 nm gap (red line) and the excitation (dashed lines) and emission (solid shadowed lines) fluorescence spectra for Alexa Fluor 647 (a) and Crystal Violet (b).

5. Luminescence background when no fluorescent dye is present



Figure S5. Intensity trace and correlation function on a silicon antenna with 20 nm gap size. No fluorescent molecule is used in this experiment to record the level of luminescence background. The 10 μ W excitation power at 633 nm is similar to the conditions used in Fig. 3a-c. No correlation is seen for lag times > 10 μ s as the curve is symmetrical around zero. For lag times < 10 μ s, the extremely low detection rate does not enable to construct any correlation function, so the correlator output remains at the -1 level.

6. Quantum yield enhancement for 20 nm silicon nanogap antenna



Figure S6. Quantum yield enhancement computed for a dipolar source oriented parallel (X) to the silicon antenna main axis. The different values ϕ_0 indicate the initial (intrinsic) quantum yield of the source. While no quantum yield enhancement is seen with a high efficiency emitter ($\phi_0 > 80\%$), using emitters with low intrinsic quantum yields maximizes the quantum yield enhancement.

7. FCS analysis of crystal violet fluorescence traces on silicon antenna



Figure S7. FCS correlation function for the fluorescence trace recorded with crystal violet on 20 nm silicon nanogap antenna with the excitation polarization parallel and perpendicular to the antenna main axis (the raw intensity traces are shown in Fig. 2a & 2c). The long correlation times in the millisecond range show that the fluorescence fluctuations for crystal violet are not limited by translational diffusion and indicate adsorption on the silicon surface.



8. Comparison of decay rates for a dipolar source parallel and perpendicular to the gap

Figure S8. Comparison of total decay rate Γ_{tot} , radiative rate Γ_{rad} and quantum yield $\Gamma_{rad}/\Gamma_{tot}$ for a dipole emitter located in the center of the silicon dimer antenna with orientation parallel (X, left column) or perpendicular (Y, right column) to the dimer main axis. All rates are normalized to the dipole's radiative rate in free space $\Gamma_{rad,0}$. The dipole with perpendicular orientation (Y) shows almost negligible radiative emission.



9. Radiation patterns for a dipolar source parallel and perpendicular to the gap

Figure S9. Comparison of radiation patterns for a dipole emitter located in the center of the silicon dimer antenna with orientation parallel (X, left column) or perpendicular (Y, right column) to the dimer main axis. The gap size is 20 nm and the emission wavelength is 670 nm. The lower graphs show the reference radiation patterns for a dipole emitter in free space. While the antenna has negligible effect on the radiation pattern for the emitter with parallel (X) orientation, the collection efficiency is reduced by 0.5x for the dipole with perpendicular (Y) orientation.

10. Reference fluorescence decay kinetics on confocal setup



Figure S10. Normalized fluorescence decay traces of Alexa Fluor 647 with 200 mM methyl viologen obtained on the confocal reference setup (green dots) and on a 20 nm gap silicon antenna with excitation light parallel (red) and perpendicular (blue) to the dimer axis. Black lines are numerical fits convoluted by the instrument response function. A single exponential decay with 350 ps lifetime is used to model the decay kinetics for the confocal reference and the antenna with perpendicular orientation.