

Photoluminescent Organosilane-Functionalized Carbon Dots as Temperature Probes

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Materials and methods

Chemicals.

3-(2-Aminoethylamino)propyltrimethoxysilane (AEAPTMS), 3-aminopropylmethyldiethoxysilane (APMDES), 3-aminopropyltriethoxysilane (APTES), 3-aminopropyltrimethoxysilane (APTMS), phenyltrimethoxysilane (PhTMS), tetraethylorthosilicate (TEOS), quinine sulfate, and sodium hydroxide were purchased from Aldrich (Milwaukee, WI, USA). Monobasic, dibasic, and tribasic sodium phosphates and sodium chloride were obtained from J. T. Baker (Phillipsburg, NJ, USA). Ultrapure water (18.2 M Ω /cm) was obtained from a Milli-Q ultrapure system. The values of pH of the phosphate solutions ranged from 2.0 to 12.0.

Synthesis of organosilane-functionalized carbon dots (SiC-dots).

Each organic silane compound of interest was mixed with water to a final concentration of 1 M and a volume of 15 mL. The solutions were heated hydrothermally in a stainless-steel autoclave at 300 °C for 2 h. The resulting light-brown solutions were cooled to room temperature and centrifuged [1006 g (3000 rpm), 10 min]. The supernatant was collected and filtered through a 0.22- μ m membrane to remove large or agglomerated particles. To further purify the as-prepared SiC-dots, each of the filtrates was mixed with water (5 mL) and subjected to dialysis against pure water through a membrane (MWCO = 3.5–5 kD, Float-A-Lyzer G2, Spectrum Laboratories, Rancho Dominguez, CA, USA) for 3 h. This approach provided transparent, light-yellowish/brown aqueous solutions containing surface-passivated SiC-dots; aqueous solutions of the as-prepared SiC-dots were stable for at least 3 months.

The QYs (ϕ) of the SiC-dots were calculated by comparing their integrated PL intensities (excitation at 365 nm) and absorbances at 365 nm with those of quinine

sulfate.^{1, 2} Quinine sulfate ($\phi_r = 0.54$) was dissolved in 0.1 M H₂SO₄ (refractive index: 1.33) and the SiC-dots were dissolved in water (refractive index: 1.33). To minimize re-absorption effects, the absorbance of each solution (in a 10-mm cuvette) at the excitation wavelength was maintained at less than 0.1. The excitation and emission slit widths were set at 5.0 nm when recording the PL spectra.

Characterization.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded using JSM-1200EX II (JEOL Ltd., Tokyo, Japan) and FEI Tecnai-G2-F20 instruments equipped with a Philips Technai G2 dispersive X-ray spectrometer. For X-ray diffraction (XRD) measurements, a PANalytical X'Pert PRO diffractometer (Almelo, Netherlands) was employed in conjunction with Cu K α radiation ($\lambda = 0.15418$ nm). Prior to XRD measurements, the SiC-dots were placed on quartz glass supports. A Raman microscopy system with a 50 \times objective (Dongwoo Optron, KyungGiDo, Korea) was used to analyze air-dried SiC-dots. A diode-pumped solid-state laser operating at 532 nm was used as the excitation source (power: 100 mW; accumulation time: 200 s). A GBC Cintra 10e double-beam UV–Vis spectrophotometer (Victoria, Australia) was used to record the UV–Vis spectra of the SiC-dots in ultrapure water. The PL spectra of the as-prepared solutions of SiC-dots and films of SiC-dots were recorded using a Cary Eclipse PL spectrophotometer (Varian, CA, USA) operated at excitation wavelengths in the ranges 360–440 and 320–420 nm, respectively. Films of SiC-dots were prepared by placing drops of a solution of SiC-dots onto a glass substrate and then drying in an oven (100 °C, 10 min). The temperature-dependence of the PL of solutions of SiC-dots was measured using a single-cell Peltier temperature controller (Varian, CA, USA). Measurements of PL intensity were made 5 min after thermal equilibration at each temperature. The

PL of the solutions of SiC-dots was monitored over a temperature range from 293 to 343 K, with an interval of 10 K. To investigate defect emission characteristics, the PL of films of SiC-dots was monitored over a temperature range from 100 to 300 K, with an interval of 25 K. The PL spectra of films of SiC-dots were recorded with excitation at 325 nm from a continuous He-Cd laser (20 mW; Plasma, Ryazan, Russia). The laser spot size on the sample was $7.1 \times 10^{-2} \text{ cm}^2$. The photostability of the solutions and films of SiC-dots were investigated under continuous illumination from the Xe lamp in a PL spectrophotometer (Varian, CA, USA). Their temperature-dependent PL lifetimes were recorded using an Edinburgh FL 900 photo-counting system (Edinburgh Instruments, Livingston, UK), with a 377-nm laser (Spectra Phys, Irvine, CA, USA) employed as an excitation source (pulse rate: 6 ns) and a 440-nm narrow bandpass filter used to minimize scattering light. A Varian 640 Fourier transform infrared (FTIR) spectrophotometer (Varian, USA) was used to analyze the as-prepared SiC-dots. X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCA210 electron spectroscopy from VG Scientific (West Sussex, UK). Binding energies were corrected by using the $4f_{7/2}$ peak at 84.0 eV as a standard. PL images of the excited films of SiC-dots were recorded using a digital camera (Nikon Corp, Japan). The index finger of a volunteer from this laboratory was partially covered with SiC-dots and dipped into water at different temperatures (277, 291, 301, and 313 K) for 1.5 min. Once the index figure was removed from the water, PL images were recorded immediately under irradiation from a UV lamp. For PL imaging, thin films of SiC-dots were fabricated by placing drops of solutions of SiC-dots onto glass substrates, which were then subjected to baking at 373 K for 10 min. PL images of these SiC-dots thin films were recorded with excitation at various wavelengths (UV: 360–370 nm; blue light: 460–490 nm; green light: 530–550 nm) at

various temperatures (293–343 K). A Hg lamp (100 W) was used as the light source; three band-pass filters were used separately to select the wavelength. The system temperature was controlled using a temperature controller (Wealtec, Taiwan).

1. Effect of Organic silanes on quantum yield and solubility of SiC-dots

In previous studies, we found that organic compounds possessing amino and carboxylate groups facilitated the preparation of highly-water-soluble, photoluminescent C-dots.³ Therefore, in this study we tested some low-cost alkoxy silane compounds possessing hydrophilic groups [3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS), 3-aminopropylmethyldiethoxy-silane (APMDES), 3-amino-propyltriethoxysilane (APTES), 3-aminopropyltrimethoxy-silane (APTMS)] for the preparation of SiC-dots. As controls, we selected hydrophobic alkoxy silane compounds [phenyltrimethoxysilane (PhTMS), tetraethylorthosilicate (TEOS)]. Table S1[†] reveals that the PL QY (42.6%) of the SiC-dots prepared from APTMS was greater than that (30.6%) of C-dots prepared from glycine or other carbon precursors.^{3, 4} Like the C-dots prepared from glycine, the as-prepared SiC-dots from APTMS were highly water-soluble. Precursors (e.g., PhTMS) containing hydrophobic functional groups led to the preparation of SiC-dots with low QYs and low water-solubility. The SiC-dots prepared from precursors (e.g., AEAPTMS, TEOS) having carbon chains longer than that in APTMS also possessed relatively lower QYs.

Table S1. Optical properties of SiC-dots prepared from various alkoxy silanes

Precursor	QY ^a (%)	λ_{ex}^b (nm)	λ_{em}^c (nm)	FWHM ^d (nm)	λ_{max}^e (nm)
AEAPTMS	12.5	320	398	90	270
APMDES	21.8	360	436	88	269
APTES	36.3	360	438	82	270
APTMS	42.6	360	432	85	270
PhTMS	2.7	320	388	86	260
TEOS	8.1	320	391	119	263

^a QYs were determined through comparison with that of quinine sulfate. ^b Maximum of excited wavelength. ^c Maximum of emission wavelength. ^d FWHM = full width at half maximum. ^e Maximum absorption wavelength.

Table S2 Nanosecond lifetimes determined from triexponential fitting of the PL decays of SiC-dot solutions at various temperatures

T(K)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
293	11.32 ± 0.1	4.33 ± 0.08	0.91 ± 0.04
303	10.43 ± 0.1	3.87 ± 0.07	0.83 ± 0.05
313	9.73 ± 0.1	3.63 ± 0.04	0.79 ± 0.05
323	9.33 ± 0.07	3.41 ± 0.04	0.68 ± 0.04
333	8.84 ± 0.1	3.08 ± 0.06	0.62 ± 0.04
343	8.34 ± 0.1	2.84 ± 0.05	0.57 ± 0.05

PL decay curves were fitted to a three-exponential function: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$

2. XRD, Raman, FTIR and EDX Spectra of SiC-dots

The X-ray diffraction (XRD) pattern of the SiC-dots (Fig. S1a[†]) displays a broad peak at a value of 2θ of 23° , revealing the amorphous nature of the carbon structure.⁵ The Raman spectra of the SiC-dots feature two broad peaks located near 1352 and 1567 cm^{-1} that are for the D (sp^3) and G (sp^2) bands, respectively (Fig. S1b[†]). The coexistence of these two bands supports an amorphous structure for the as-prepared SiC-dots. The as-prepared SiC-dots were highly soluble in aqueous solution, suggesting the presence of hydrophilic functional groups on their surfaces. The Fourier transform infrared (FTIR) spectrum of the SiC-dots (Fig. S1c[†]) reveals absorption bands near 3400 cm^{-1} for the N–H and O–H stretching vibrations of the amino and hydroxyl groups and an absorption band at 1630 cm^{-1} representing the stretching vibration of C=O groups, the existence of which implies that the APTMS units on the surfaces of the SiC-dots were partially oxidized.⁶ We assign the bands located in the region from 1350 to 1450 cm^{-1} to CH_2 stretching vibrations and the two signals at 1010 and 1090 cm^{-1} to Si–O–Si and Si–O–C vibrations, respectively, confirming the presence of Si atoms, as supported by the energy-dispersive X-ray spectroscopy (EDX) results (Fig. S1d[†]).

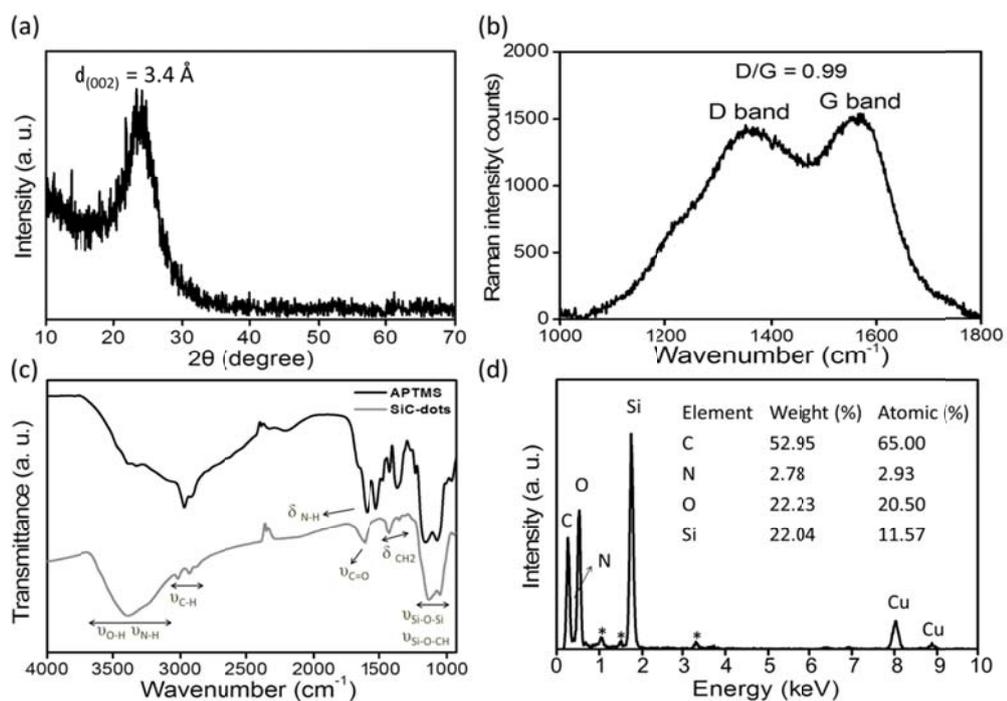


Figure S1. (a) XRD pattern, (b) Raman spectrum, (c) FTIR (d) EDX spectrum of SiC-dots prepared from APTMS. Peaks identified by asterisks in (d) are background signals from the system.

3. X-Ray photoelectron spectroscopy (XPS) of the SiC-dots

X-ray photoelectron spectroscopy (XPS) measurement of SiC-dots revealed peaks from the C_{1s}, N_{1s}, O_{1s}, O_{2s}, Si_{2s}, and Si_{2p} core levels (Fig. S2a[†]).⁷ The C_{1s} spectrum (Fig. S2b[†]) shows four peaks at 284.5, 285.6, 286.6, and 287.9 eV, which are attributed to C=C, C-N, C-OH, and C=O, respectively.^{6,8} The presence of C=O/C-N signals coincided with FTIR data, further revealing the existence of polar groups such as NH₂ in the surfaces of SiC-dots.

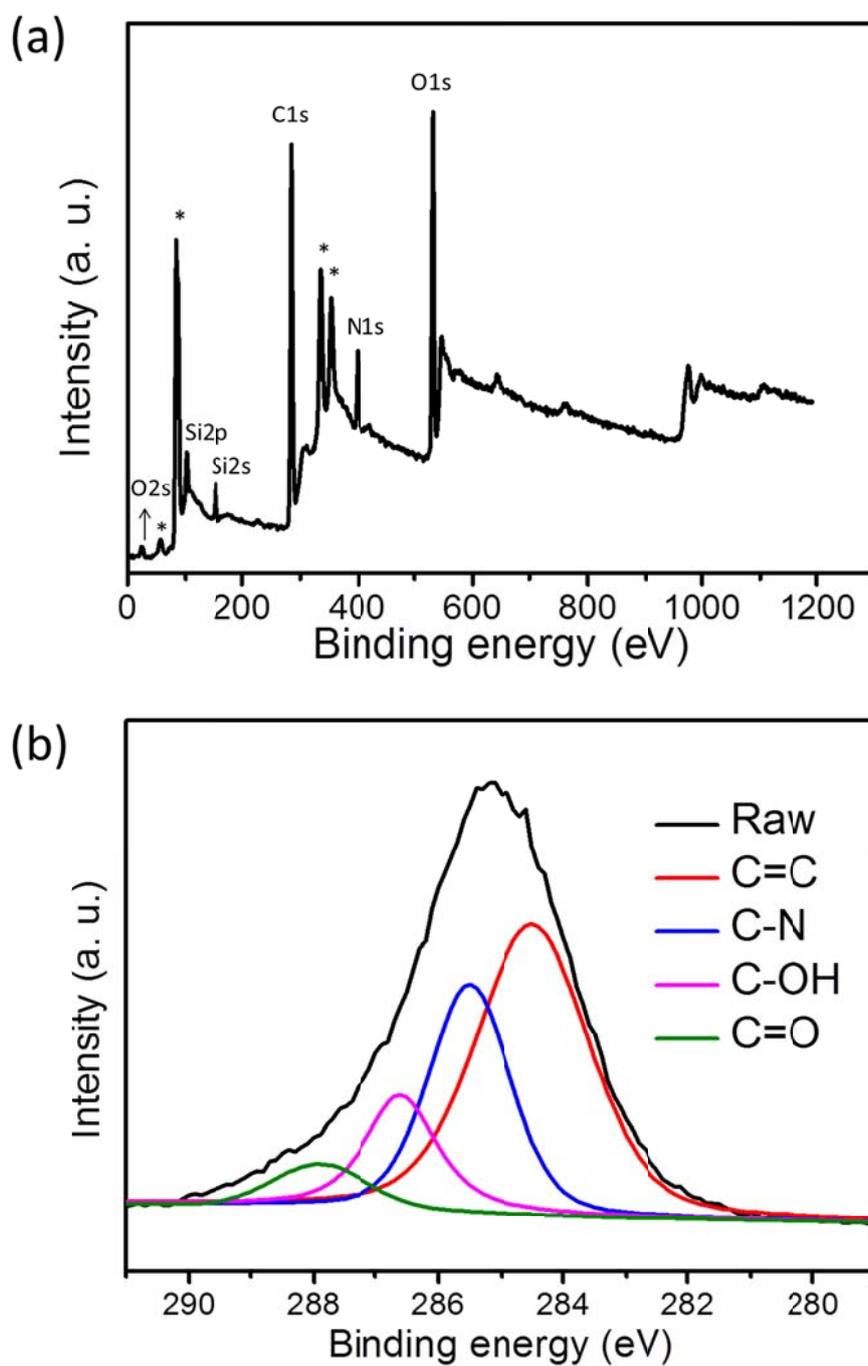


Figure S2. (a) XPS spectrum and (b) C_{1s} spectra of SiC-dots. Binding energies were corrected by using the 4f_{7/2} peak at 84.0 eV as a standard. Peaks identified by asterisks in (a) are signals from Au.

4. Optical properties of the SiC-dots

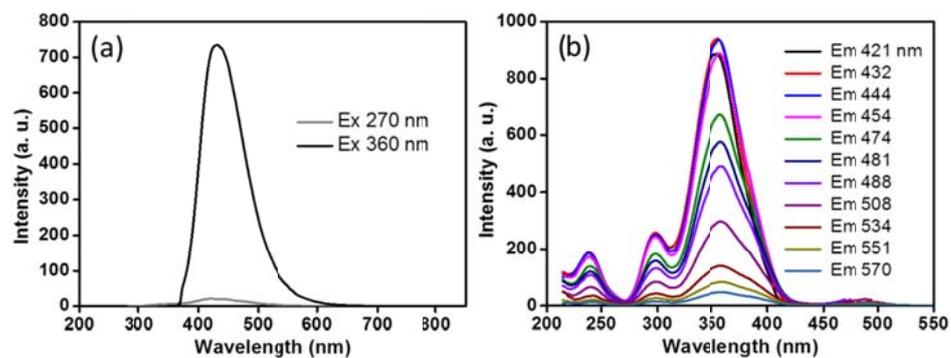


Figure S3. (a) Emission and (b) Excitation spectra of SiC-dots solution.

5. Stability of SiC-dots

The PL intensity remained almost constant (a decrease of less than 3%) in solutions of the SiC-dots containing NaCl at concentrations of up to 500 mM; (Fig. S4a[†]). The PL intensity of our SiC-dots did not change significantly under continuous illumination with an Xe lamp for up to 6 h (Fig. S4b[†]). In addition, we observed pH-independent behavior of the PL intensities of the SiC-dots over the pH range from 2.0 to 12.0 (Fig. S4c[†]).

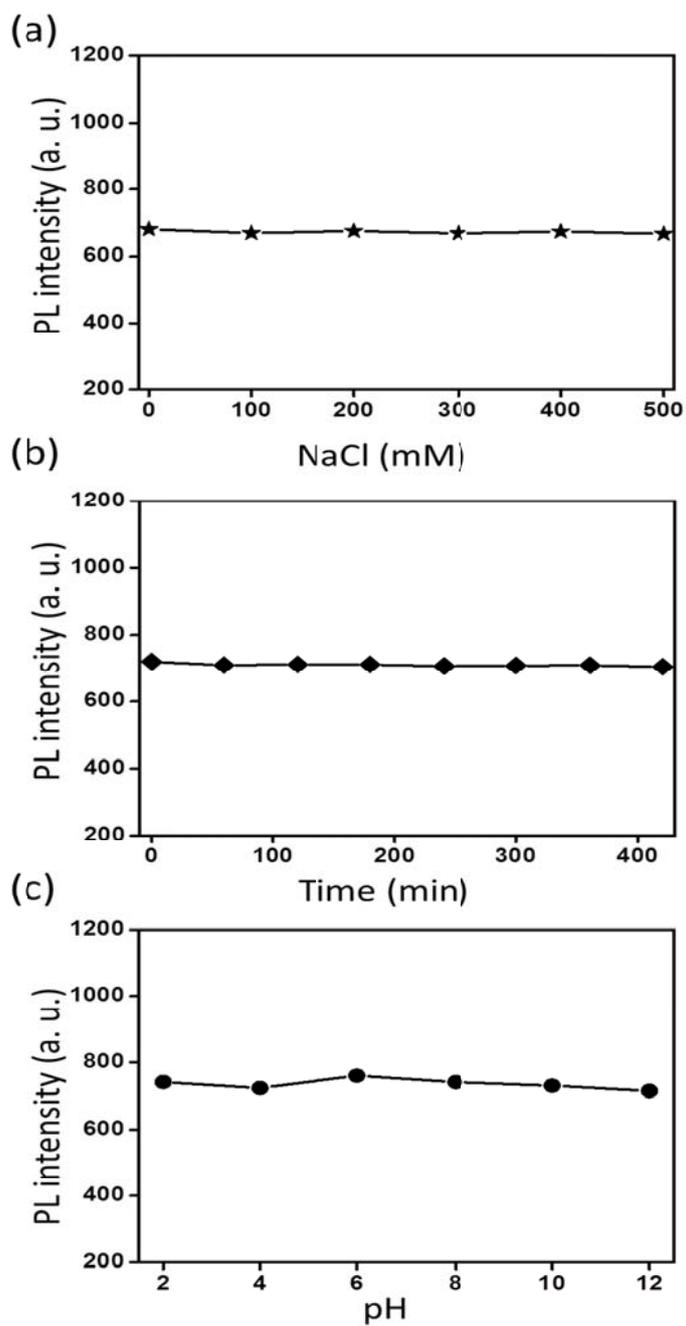


Figure S4. Effects of (a) NaCl concentration; (b) illumination with an Xe lamp; and (c) pH on the stability of SiC-dots. Excitation and emission wavelengths: 360 and 432 nm, respectively. SiC-dot were prepared in (a) phosphate buffers (5 mM, pH 7.4) containing various concentrations of NaCl, (b) phosphate buffer (5 mM, pH 7.4), and (c) phosphate solutions (5 mM) at values of pH from 2.0 to 12.0.

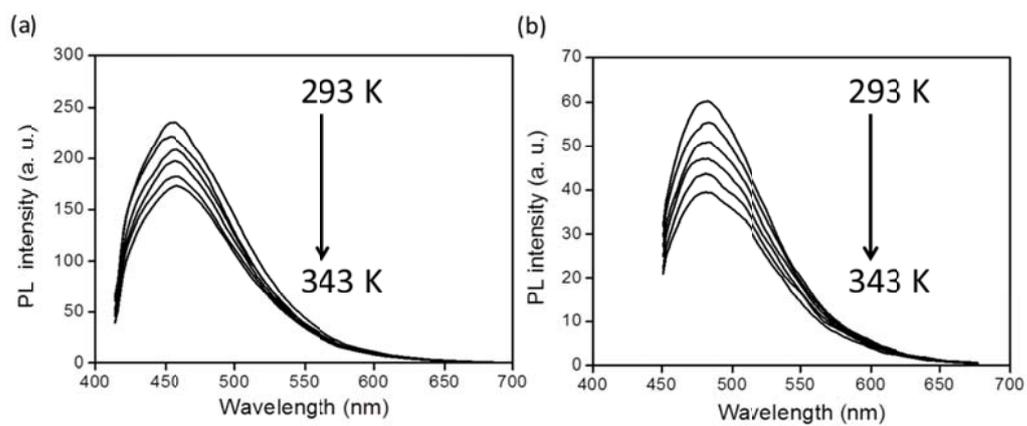


Figure S5. PL spectra of a SiC-dot solution at various temperatures from 293 to 343 K, with an interval of 10 K. Excitation wavelengths: (a) 400 and (b) 440 nm.

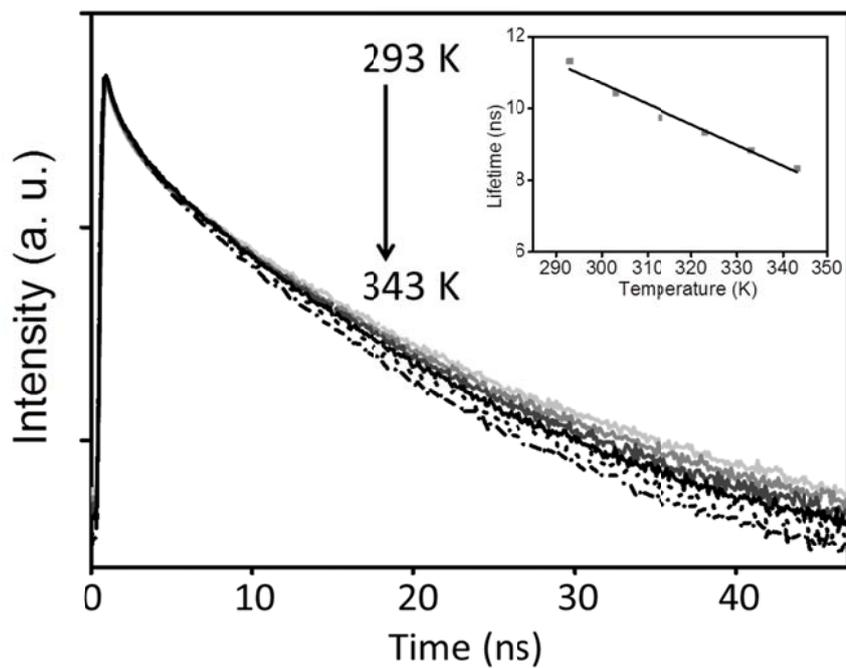


Figure S6. PL decay curves of a SiC-dot solution at various temperatures from 293 to 343 K, with an interval of 10 K. Inset: plot of τ of SiC-dot solution against temperature.

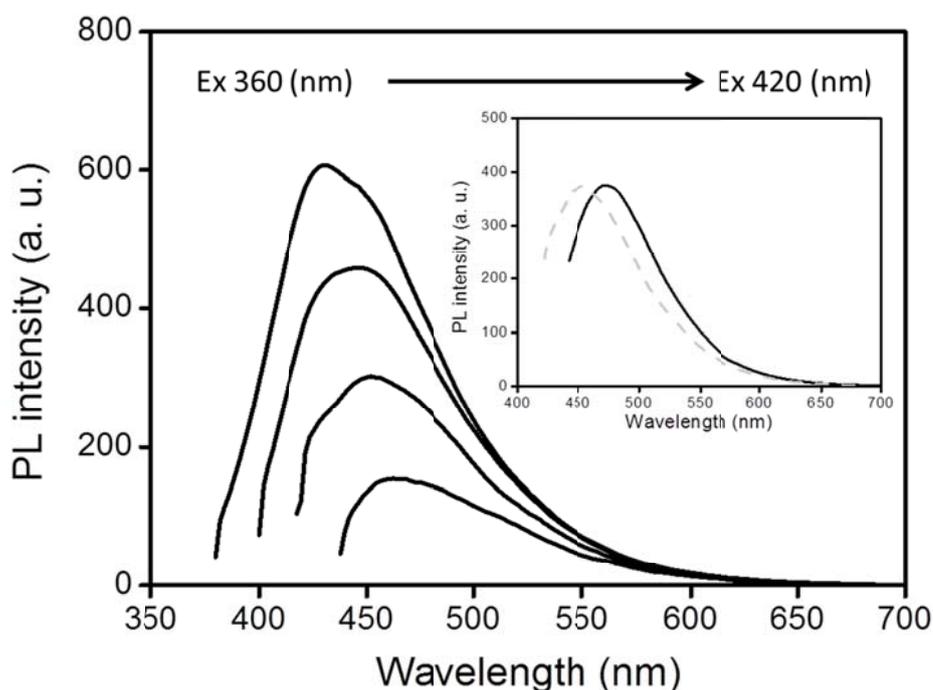


Figure S7. PL spectra of a representative SiC-dot film excited at wavelengths from 360 to 420 nm, with a 20-nm increment. Inset: PL spectra of a SiC-dot film (dotted curve) and a SiC-dot solution (solid curve) excited at 420 nm.

References

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