

Supporting information

Size-tunable silicon nanoparticles synthesized in solution via a redox reaction

Megan A. Parker, Maria Letizia De Marco, Alexander Castro-Grijalba, Anissa Ghoridi, David Portehault, Stanislav Pechev, Elizabeth A. Hilar, Sabrina Lacomme, Aurélie Bessi re, Fr d rique Cunin, Patrick Rosa, Mathieu Gonidec, Glenna L. Drisko

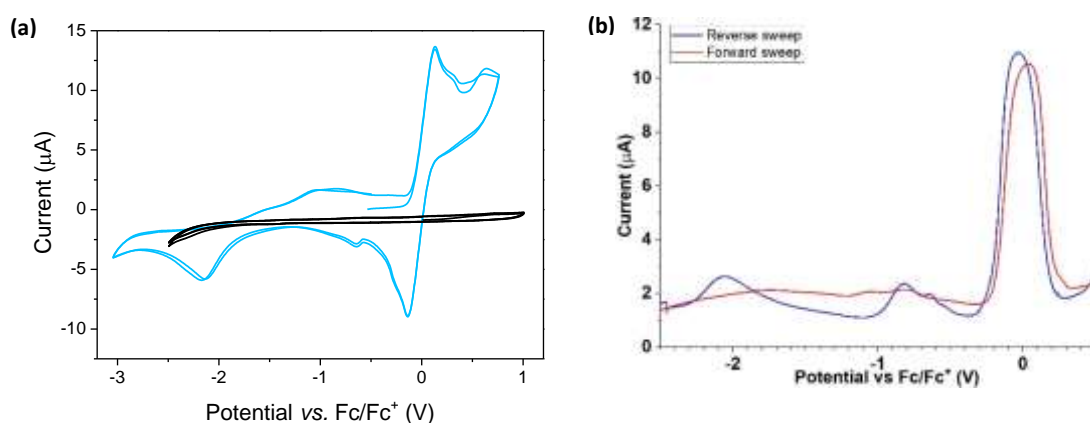


Figure S1. (a) Cyclic voltammogram (scan rate, 100 mV s^{-1} , potential corrected vs Fc/Fc^+) of 5.0 mg silicon bisamidinate **2** and 8.2 mg of ferrocene (7.6 eq) in DMF/0.1 M TBAPF₆ solution vs (Fc/Fc^+) using a platinum disk working electrode, shown in red, with the baseline shown in black. (b) Square wave voltammograms in reverse (blue curve) and forward (red curve) modes (scan rate 50 mVs^{-1}). Integration of the irreversible peak seen for **2** gives a charge count close to 1/7 of the ferrocene peak, supporting a monoelectronic process

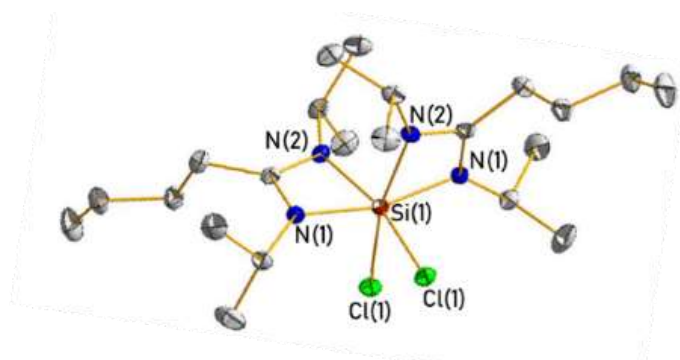


Figure S2. Molecular structure of **2** with anisotropic displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table S1. Single-crystal X-ray diffraction data collection and refinement information for compound **2**.

Formula	C ₂₂ H ₄₆ Cl ₂ N ₄ Si
<i>D</i> _{calc.} / g cm ⁻³	1.139
<i>μ</i> /mm ⁻¹	0.298
Formula weight	465.62
Color	colorless
Shape	plate-shaped
Size/mm ³	0.169 × 0.12 × 0.041
<i>T</i> / K	120
Crystal System	monoclinic
Space Group	<i>C2/c</i>
<i>a</i> /Å	13.1108(12)
<i>b</i> /Å	12.0581(11)
<i>c</i> /Å	18.0846(16)
<i>α</i> /°	90
<i>β</i> /°	108.199(3)
<i>γ</i> /°	90
<i>V</i> /Å ³	2716.0(4)
<i>Z</i>	4
<i>Z'</i>	0.5
Wavelength / Å	0.71073
Radiation type	MoK _α
2 θ range for data collection/°	4.702 to 56.564
Index ranges	-17 ≤ <i>h</i> ≤ 17, -16 ≤ <i>k</i> ≤ 16, -24 ≤ <i>l</i> ≤ 24
Measured Refl's.	13089
Indep't Refl's	3365
<i>R</i> _{int}	0.0490
Refl's [<i>I</i> ≥ 2 σ (<i>I</i>)]	2551
Data/restraints/parameters	3365/0/137
Goof	1.034
wR ₂ (all data)	0.0810
wR ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0734
<i>R</i> ₁ (all data)	0.0550
<i>R</i> ₁ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0330
Largest Peak / e Å ⁻³	0.311
Deepest Hole / e Å ⁻³	-0.223

Table S2. Distortion parameters calculated with the OCTADIST software¹ for compound **2**.

<i>d</i> _{mean} (Å)	1.9853
ζ (Å)	0.896439
Δ	0.006508
Σ (°)	87.3007
Θ (°)	282.0027

ζ and Δ are radial distortion parameters: $\zeta = \sum_{i=1}^6 |d_i - d_{mean}|$ and $\Delta = \frac{1}{6} \sum_{i=1}^6 \left(\frac{d_i - d_{mean}}{d_{mean}} \right)^2$, where *d*_{*i*} are the individual Si-ligand bond lengths and *d*_{mean} their average.

Σ is an angular distortion parameter: $\Sigma = \sum_{i=1}^{12} |90 - \varphi_i|$, where φ_i are the 12 ligand-Si-ligand angles.

Θ is a torsional distortion parameter: $\Theta = \sum_{i=1}^{24} |60 - \theta_i|$, where θ_i are the 25 angles between two vectors of opposed twisting faces.

Table S3. Continuous Shape Measure calculated with the online CoSyM tool² for compound **2**. The C₂ symmetry point group and octahedral shape were chosen for the calculations. Note that for both measures, values range from 0 (perfect agreement with symmetry or shape) to 100.

C ₂ Symmetry	9.99E-13
Octahedron	2.908108
Chirality	1.647677

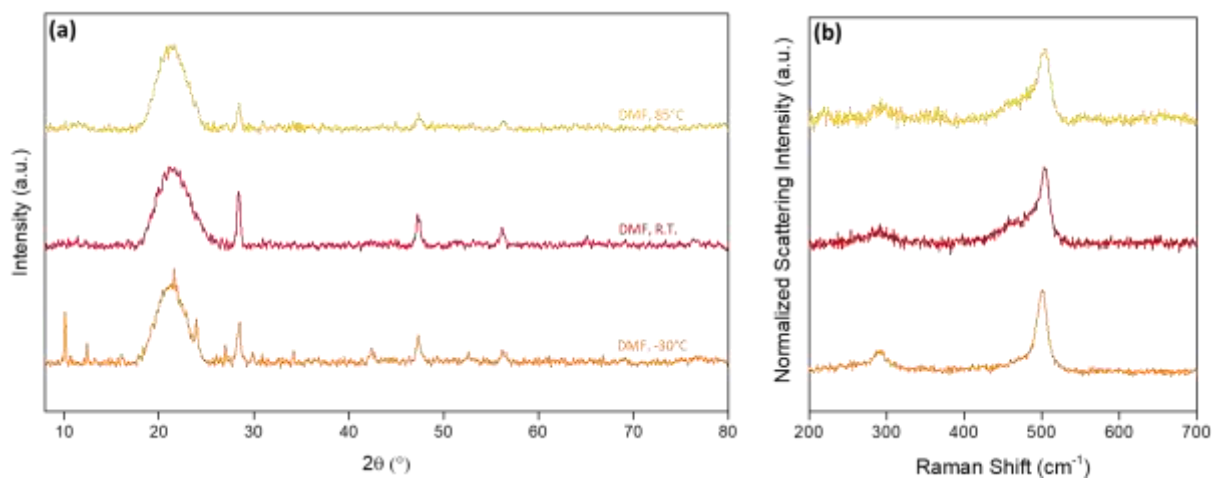


Figure S3. (a) Powder X-Ray diffractograms and (b) Raman spectra of reaction products from silicon bisamidinate **2** + Na₄Si₄ stirred in DMF for 16 h at (orange) -30 °C, (red) 25 °C, and (yellow) 85 °C.

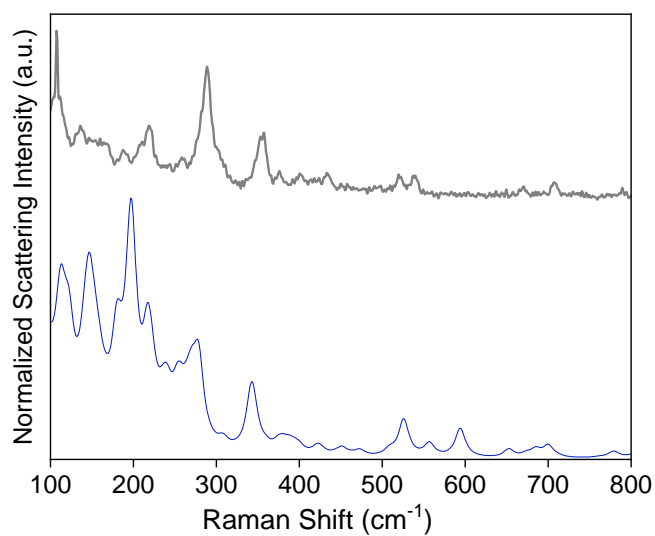


Figure S4. Superposition of (grey) the experimental and (blue) the DFT computed Raman spectra of silicon bisamidinate, **2**.

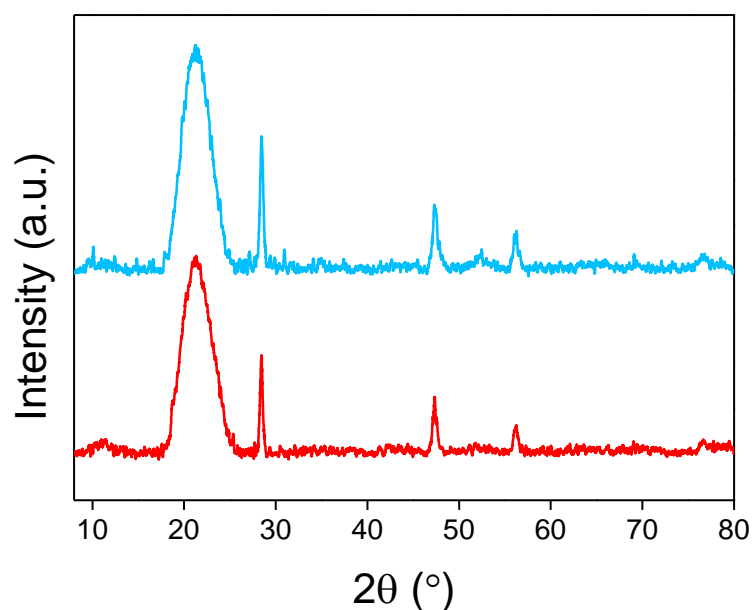


Figure S5. Full X-ray diffractogram of particles produced in (blue) DMF and (red) toluene.

$$L = \frac{\lambda}{\beta \cos\theta}$$

Equation S1

$$\beta_{Total} = \beta_{Instrument} + \beta_{Sample}$$

Equation S2

Equation S1-2. Equation S1 is the Scherrer Equation, where L is the coherent domain length, the wavelength (λ) is 1.54056 Å for $\text{CuK}\alpha_1$ radiation, θ is the Bragg diffraction angle and β is the line integral breadth broadening, corrected using the Lorentzian profile approximation (Equation S2) to take into account for the instrumental broadening.

Table S4. Calculated coherent domain lengths based on XRD powder pattern integral breadths of the diffraction peak values using the Scherrer Equation. Average values from the 220 and 311 peak calculated in red compared to actual median particle sizes. The coherent domain length for the 111 peak was omitted in the average due to interference from the capillary.

Solvent	Calculated Coherent Domain Length (nm)			Coherent Domain Length Avg (nm)	Actual median particle size from TEM (nm)
	111	220	311		
DMF	26.5	14.1	17.2	15.6	15.8 ± 5.3
Toluene	25.6	25.0	18.8	21.9	44.0 ± 14.4

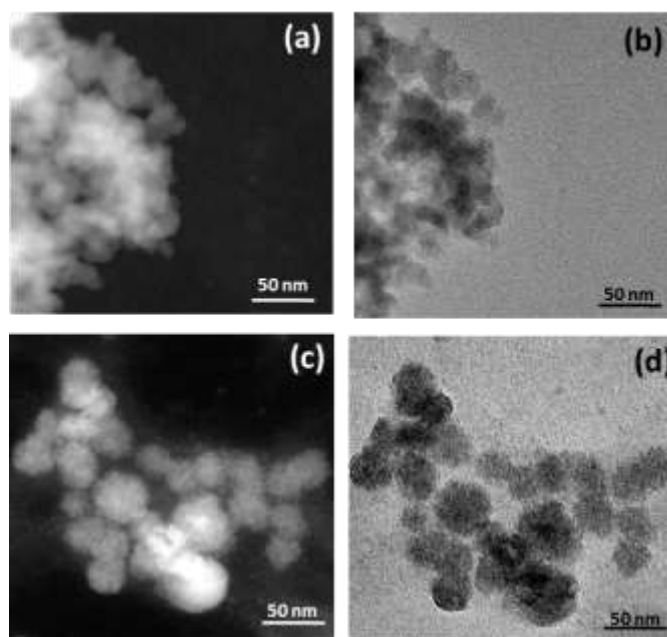


Figure S6. Dark field and corresponding bright field images of particles produced in (a, b) DMF and (c, d) toluene.

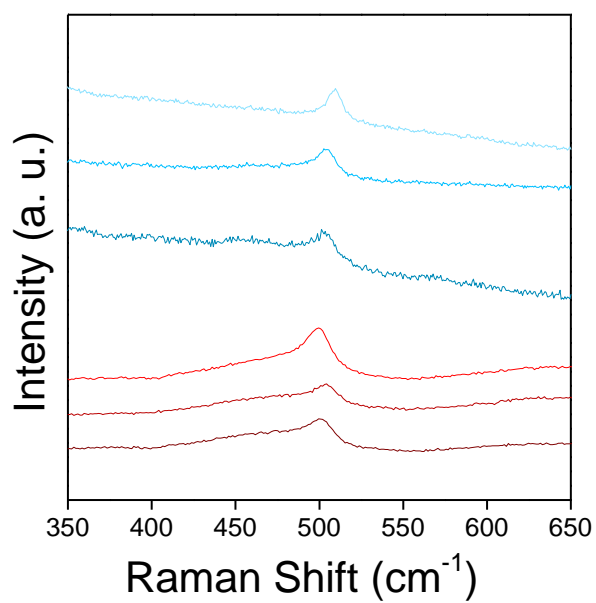


Figure S7. Raman spectra of three additional zones for the samples produced in DMF (blues) and toluene (reds).

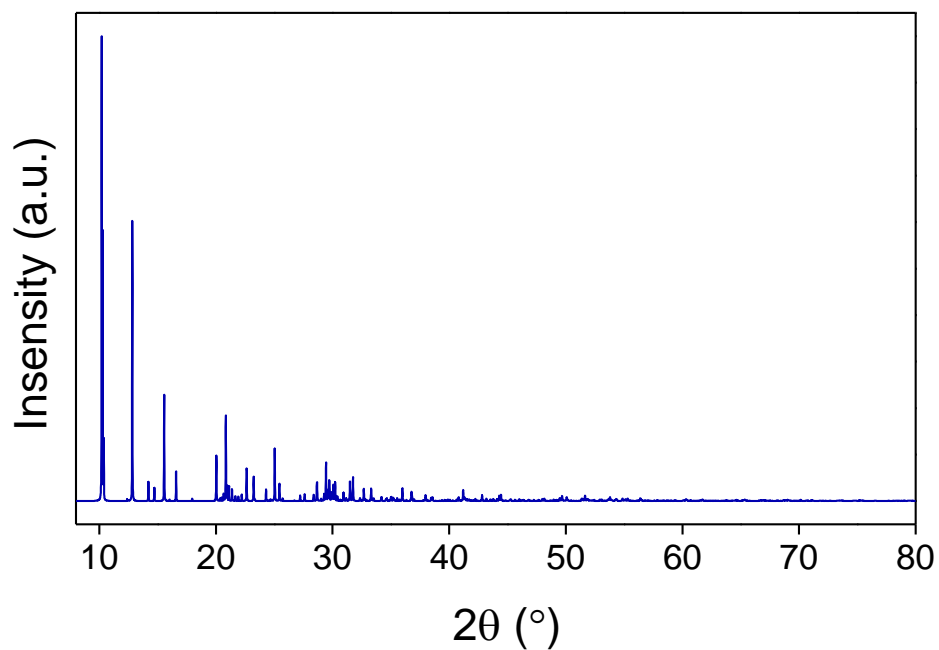


Figure S8. Simulated powder X-ray diffractogram of Silicon bisamidinate complex 2.

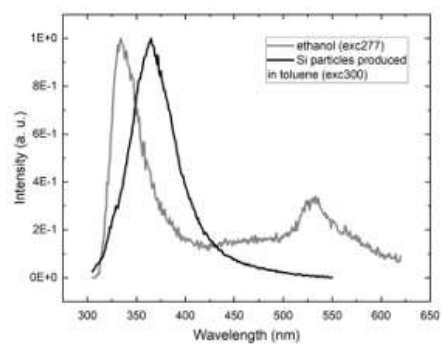


Figure S9. Normalized photoluminescence emission spectra of ethanol and of the silicon nanoparticles suspended in ethanol excited at 277 nm and 300 nm, respectively.

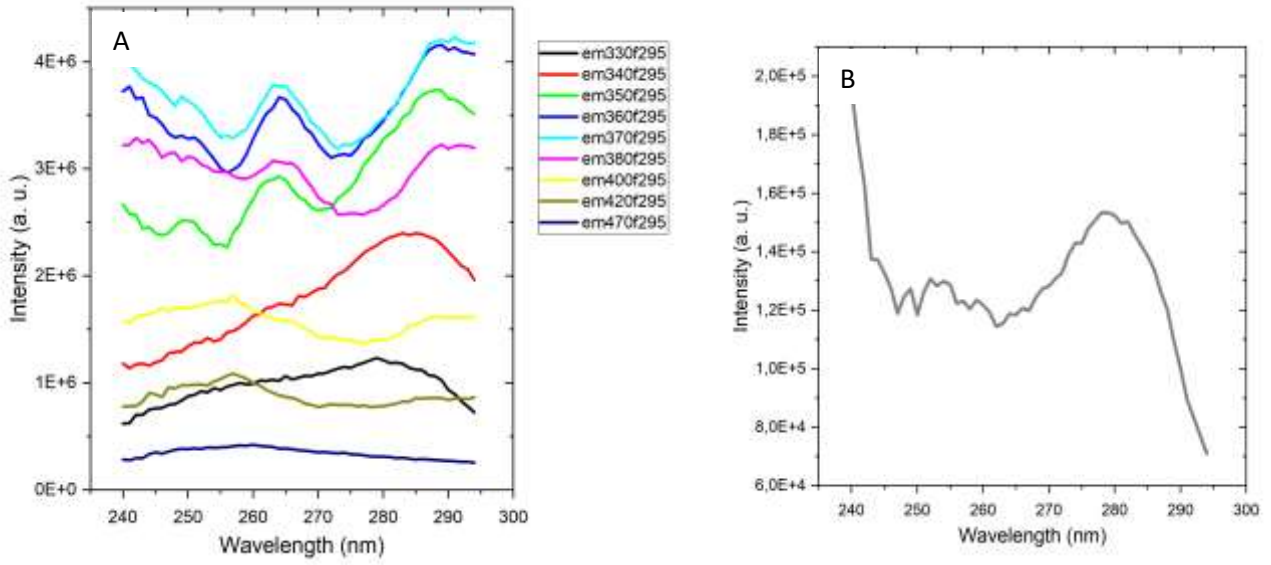


Figure S10. Excitation spectra of (A) silicon nanoparticles produced in toluene, recorded at various emission wavelength, and (B) ethanol, recorded at 332 nm.

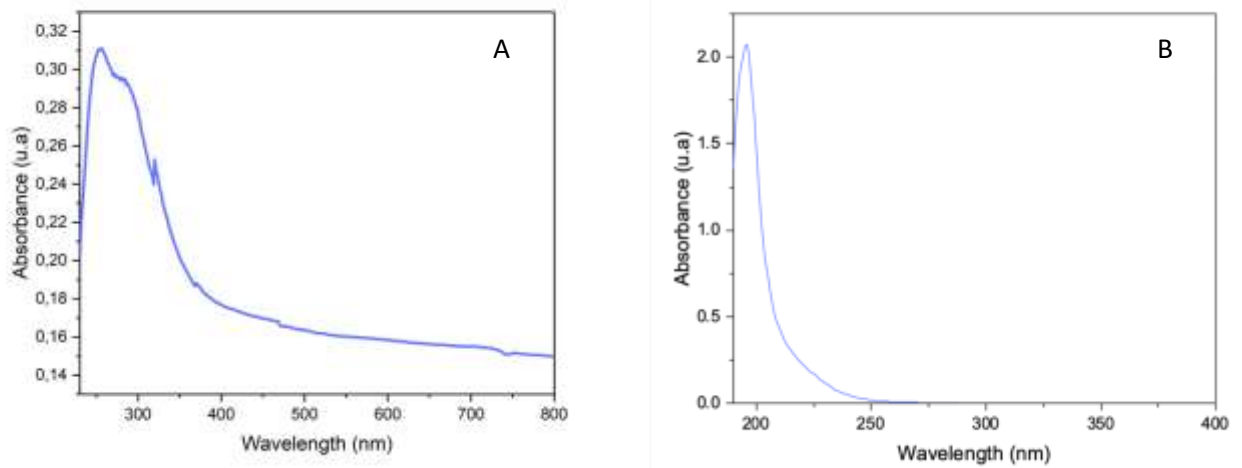


Figure S11. UV-vis absorption spectra of (A) the silicon nanoparticles produced in toluene, and of (B) ethanol.

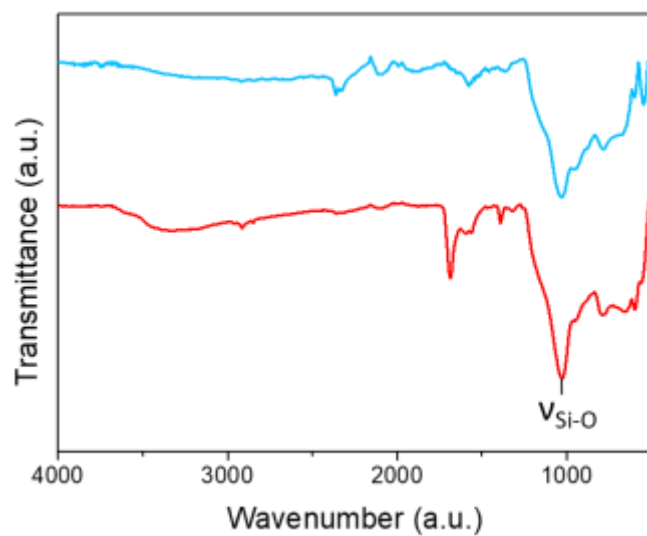


Figure S12. FTIR of particles produced in (blue) DMF and (red) toluene.

References

1. R. Ketkaew, Y. Tantirungrotechai, P. Harding, G. Chastanet, P. Guionneau, M. Marchivie, and D. J. Harding, *Dalton Trans.*, 2021, **50**, 1086.
2. S. Alvarez, *Chem. Rev.*, 2015, **115**, 13447.