Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: The Effect of Particle Size on the Optical and Electronic Properties of Hydrogenated Silicon Nanoparticles

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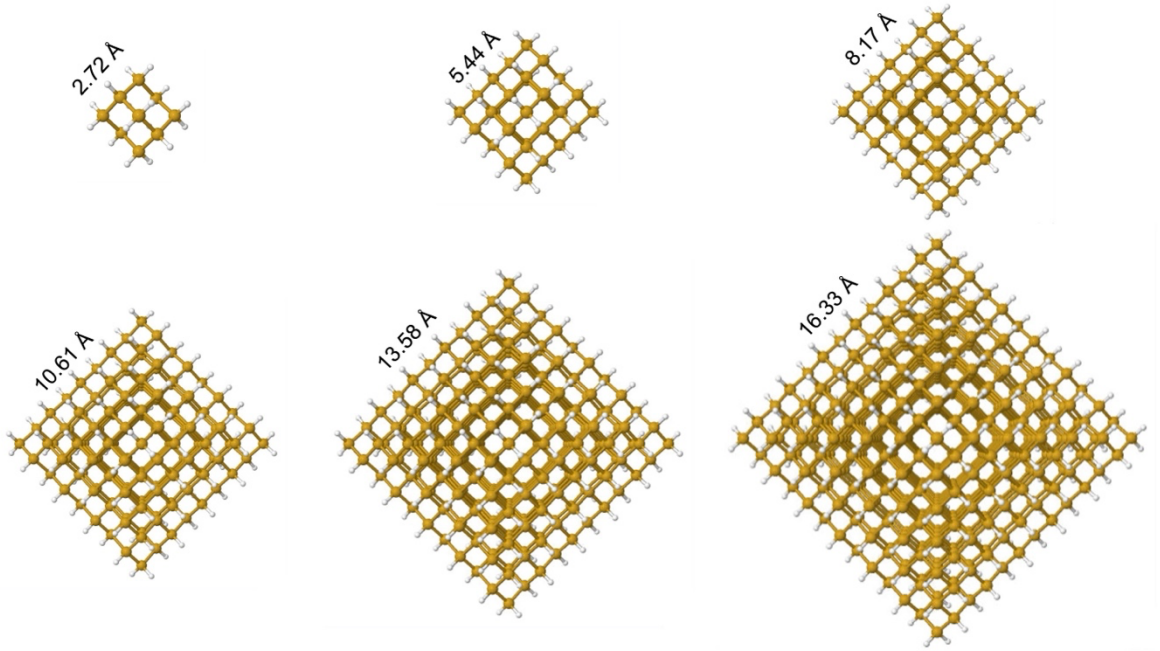

Fig S1: *DFT optimised geometries (D2 symmetry, def2-SVP, B3LYP) of the hydrogen-terminated octahedral silicon nanoparticles (SiNPs) studied here. From left to right, top line:* $Si_{10}H_{16}$, $Si_{35}H_{36}$, $Si_{84}H_{64}$. *From left to right, bottom line:* $Si_{165}H_{100}$, $Si_{284}H_{144}$, $Si_{455}H_{195}$. *Structures are scaled to the smallest structure for size comparison. Radii for all particles given in the labels.*

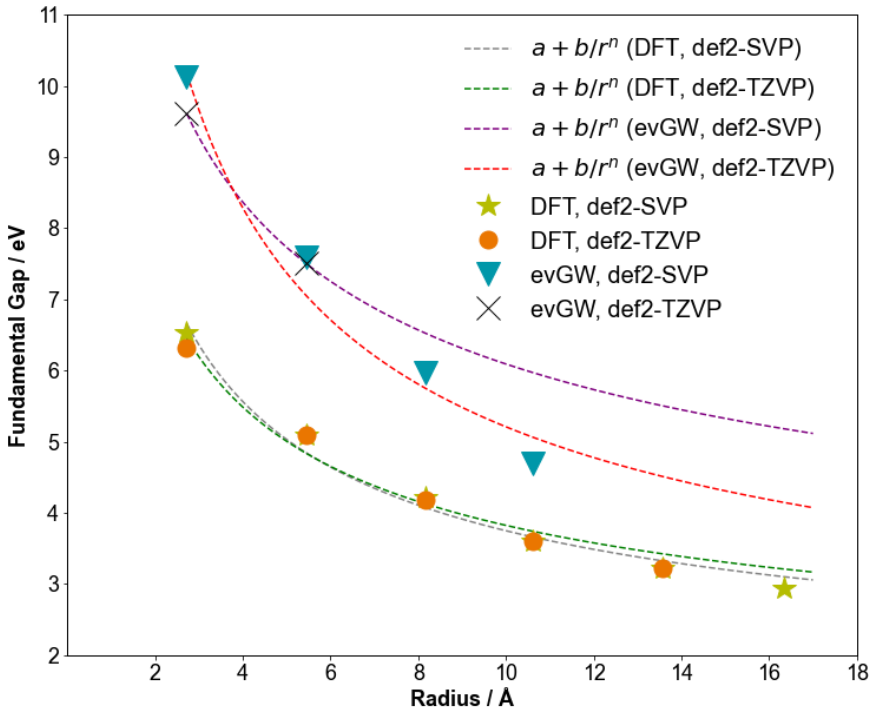

Fig S2. *Dependence of the fundamental gap on the SiNP radius calculated using DFT, def2-SVP (bright green stars) and def2-TZVP (orange circles), and evGW, def2-SVP (blue triangles) and def2-TZVP (black crosses) where tractable (i.e. those SiNPs up to $Si_{165}H_{100}$). Fits to the DFT data (grey dashed line for def2-SVP and dark green dashed line for def2-TZVP) and to the evGW (purple dashed line for def2-SVP and red dashed line for def2-TZVP) are also shown. Fitting parameters can be found in Table S9.*

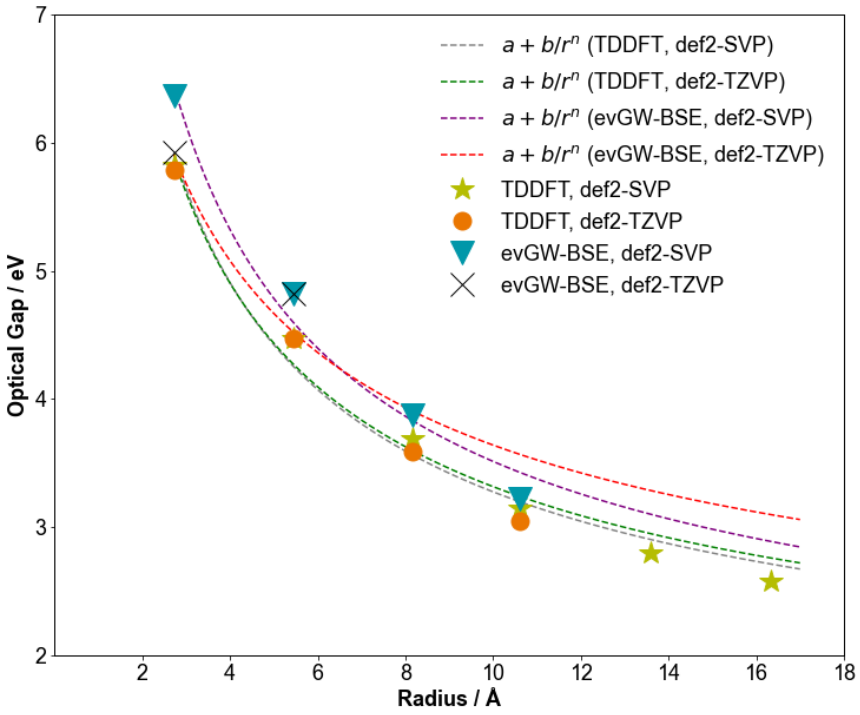

Fig S3. *Dependence of the optical gap on the SiNP radius using for $Si_{10}H_{16}$, the lowest bright excitation calculated using TDDFT, def2-SVP (bright green stars) and def2-TZVP (orange circles), and evGW-BSE, def2-SVP (blue triangles) and def2-TZVP (black crosses) where tractable. Fits to the DFT data (grey dashed line for def2-SVP and dark green dashed line for def2-TZVP) and to the evGW (purple dashed line for def2-SVP and red dashed line for def2-TZVP) are also shown. Fitting parameters can be found in Table S10.*

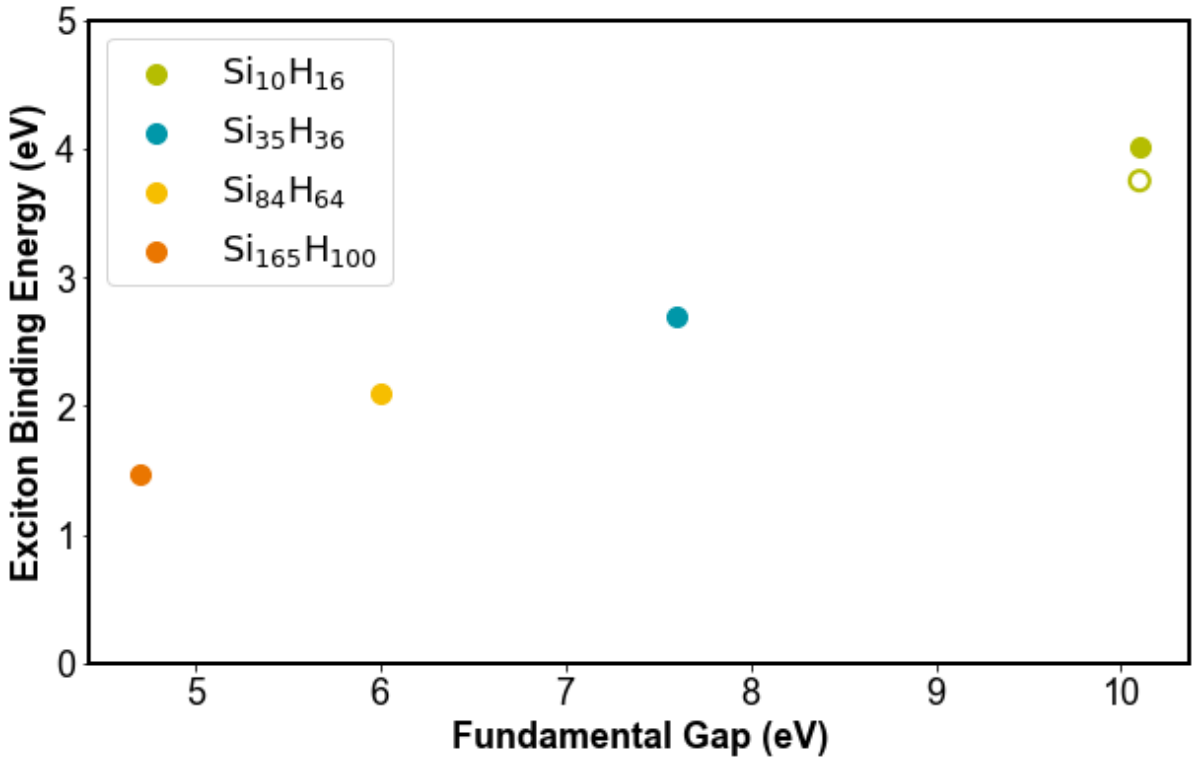

Fig S4: *Dependence of the exciton binding energy calculated via evGW/evGW-BSE (def2-SVP) on the fundamental gap calculated via ewGW-BSE (def2-SVP) for the lowest excitations of the four smallest SiNPs. The open symbol for $Si_{10}H_{16}$ indicates the exciton binding energy which was calculated using the lowest bright excited state.*

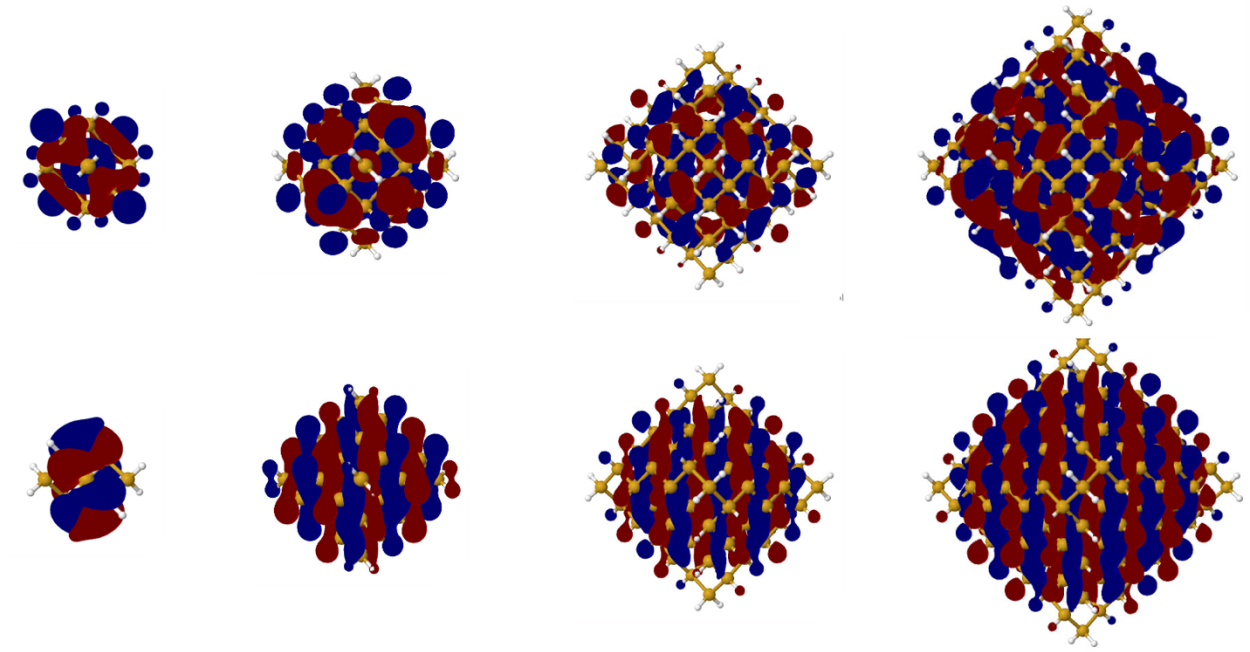

Fig S5: *Natural transition orbitals of $Si_{10}H_{16}$ to $Si_{165}H_{100}$ obtained from TDDFT calculations (D2 symmetry, def2-SVP, B3LYP). Occupied orbitals are shown in the top row, virtual orbitals in the bottom row. The occupied orbital is triply degenerate and only one of the three degenerate orbitals is shown per particle. Structures are scaled to the smallest structure from Fig S1 for comparison.*

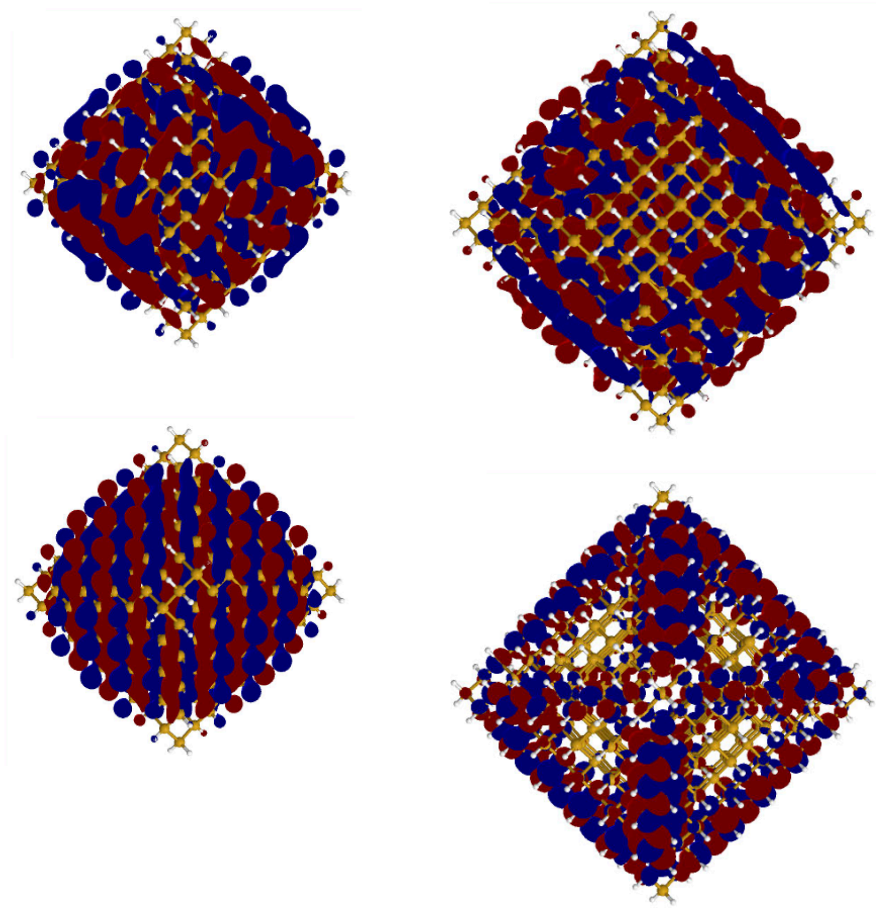

Fig S6: *NTOs of $Si_{286}H_{164}$ and $Si_{455}H_{195}$ from TDDFT calculations (D2 symmetry, def2-SVP, B3LYP). Occupied orbitals are shown in the top row, virtual orbitals in the bottom row. The occupied orbital is triply degenerate and only one of the three degenerate orbitals is shown per particle. Structures are scaled to the smallest structure from Fig S1 for comparison.*

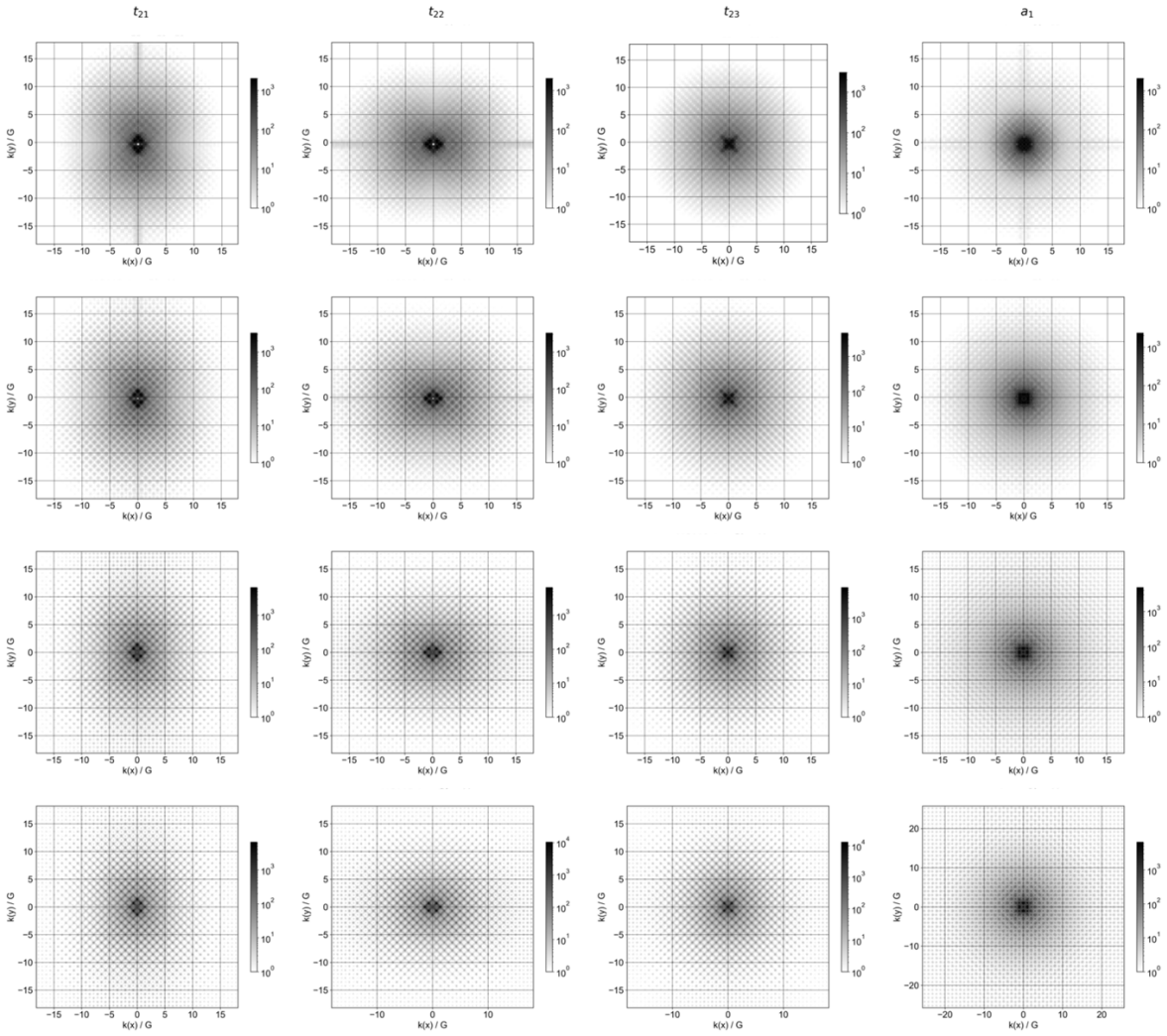

Fig S7: *Fourier transforms of the three degenerate HOMO orbitals and the LUMO orbital obtained from DFT for the first four SiNPs. First row: $Si_{10}H_{16}$. Second row: $Si_{35}H_{36}$. Third row: $Si_{84}H_{64}$. Fourth row: $Si_{165}H_{100}$.*

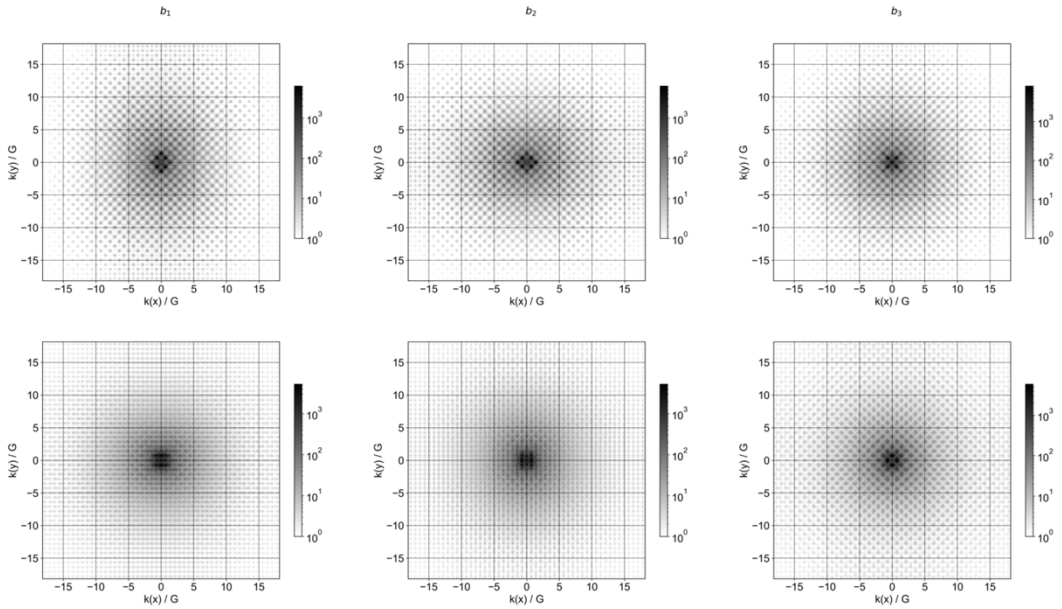

Fig S8: *Fourier transforms of the three degenerate occupied NTOs of $Si_{165}H_{100}$ (top row) and the three degenerate unoccupied NTOs of $Si_{165}H_{10}$ (bottom row) as calculated using TDDFT.*

Table S1: *Kohn-Sham (KS) highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) and the KS HOMO-LUMO gap values as calculated using DFT and highest occupied (–IP) and lowest unoccupied (–EA) quasiparticle states and the fundamental gap (Δ_f) as calculated using evGW-BSE. All results obtained using the def2-SVP basis-set. All values in eV.*

Simulation details		**DFT**			**evGW**		
Nanoparticle	**Symmetry**	**KS-HOMO**	**KS-LUMO**	**KS-Gap**	**-IP**	**-EA**	**Δ_f**
$Si_{10}H_{16}$	**D_2**	-7.54	-1.00	6.54	-9.21	0.91	10.12
	T_d	-7.54	-1.00	6.54			
$Si_{35}H_{36}$	**D_2**	-6.73	-1.63	5.1	-7.77	-0.17	7.6
	T_d	-6.73	-1.63	5.1			
$Si_{84}H_{64}$	**D_2**	-6.29	-2.07	4.22	-6.94	-0.97	5.97
	T_d	-6.29	-2.07	4.22			
$Si_{165}H_{100}$	**D_2**	-6.00	-2.39	3.61	-6.36	-1.67	4.69
	T_d	-6.00	-2.49	3.51			
$Si_{286}H_{144}$	**D_2**	-5.81	-2.59	3.22			
	T_d	-5.81	-2.59	3.22			
$Si_{455}H_{195}$	**T_d**	-5.68	-2.74	2.94			

Table S2: *Kohn-Sham (KS) highest-occupied molecular orbital (HOMO) and Lowest-unoccupied molecular orbital (LUMO) and the KS HOMO-LUMO gap values as calculated using DFT, and the highest occupied (–IP) and lowest unoccupied (–EA) quasiparticle states and fundamental gap (Δ_f) as calculated using evGW-BSE. All results obtained using the def2-TZVP basis-set. All values in eV.*

Simulation details		**DFT**			**evGW**		
Nanoparticle	**Symmetry**	**KS-HOMO**	**KS-LUMO**	**KS-Gap**	**-IP**	**-EA**	**Δ_f**
$Si_{10}H_{16}$	**D_2**	-7.54	-1.16	6.32	-9.29	0.33	9.62
	T_d	-7.54	-1.16	6.32			
$Si_{35}H_{36}$	**D_2**	-6.73	-1.63	5.10	-7.74	-0.23	7.51
	T_d	-6.73	-1.63	5.10			
$Si_{84}H_{64}$	**D_2**	-6.29	-2.10	4.19			
	T_d	-6.29	-2.10	4.19			
$Si_{165}H_{100}$	**D_2**	-6.02	-2.48	3.61			
	T_d	-6.02	-2.48	3.61			
$Si_{286}H_{144}$	**D_2**	-5.81	-2.59	3.22			
	T_d	-5.81	-2.59	3.22			

Table S3: *Energies of the highest occupied (–IP) and lowest unoccupied (–EA) quasiparticle states and fundamental gap (Δ_f) values as calculated using qsGW in combination with the def2-SVP basis set. All values in eV.*

Simulation details	**qsGW**		
Nanoparticle	**-IP**	**-EA**	**Δ_f**
$Si_{10}H_{16}$	-9.42	0.69	10.11
$Si_{35}H_{36}$	-8.08	-0.49	7.59

Table S4: *Energies of the highest occupied (–IP) and lowest unoccupied (–EA) quasiparticle states and fundamental gap (Δ_f) values as calculated using qsGW in combination with the def2-TZVP basis set. All values in eV.*

Simulation details	**qsGW**		
Nanoparticle	**-IP**	**-EA**	**Δ_f**
$Si_{10}H_{16}$	-9.46	0.31	9.77
$Si_{35}H_{36}$	-8.18	-0.87	7.31

Table S5: *Energies of the highest occupied (–IP) and lowest unoccupied (–EA) quasiparticle states and fundamental gap (Δ_f) values as calculated using G_0W_0 in combination with the def2-SVP basis set. All values in eV.*

Simulation details	**G_0W_0**		
Nanoparticle	**-IP**	**-EA**	**Δ_f**
$Si_{10}H_{16}$	-7.54	-1.00	6.54
$Si_{35}H_{36}$	-6.73	-1.63	5.10
$Si_{84}H_{64}$	-6.29	-2.07	4.22

Table S6: Energies of the *highest occupied (–IP) and lowest unoccupied (–EA) quasiparticle states and fundamental gap (Δ_f) values as calculated using G_0W_0 in combination with the def2-TZVP basis set. All values in eV.*

Simulation details	G_0W_0		
Nanoparticle	-IP	-EA	**Δ_f**
$Si_{10}H_{16}$	-7.48	-1.14	6.34
$Si_{35}H_{36}$	-6.74	-1.77	4.96

Table S7: *Optical gap values (**Δo**) as calculated using TDDFT, evGW-BSE, qsGW-BSE and G_0W_0-BSE in combination with the def2-SVP basis set. All values in eV. For $Si_{10}H_{16}$, for which the lowest excited state is not optically allowed, the gap towards the lowest bright excited state is given in between parentheses.*

Simulation details		**TDDFT**	**evGW-BSE**	**qsGW-BSE**	**G0W0-BSE**
Nanoparticle	**Symmetry**	Δo	Δo	Δo	Δo
$Si_{10}H_{16}$	D_2	5.72 (5.82)	6.19 (6.37)	6.17 (6.43)	5.68 (5.86)
	T_d	5.81			
$Si_{35}H_{36}$	D_2	4.47	4.82	4.85	4.43
	T_d	4.47			
$Si_{84}H_{64}$	D_2	3.69	3.87		3.58
	T_d	3.69			
$Si_{165}H_{100}$	D_2	3.15	3.22		3.00
	T_d	3.15			
$Si_{286}H_{144}$	D_2	2.8			
	T_d	2.8			
$Si_{455}H_{195}$	T_d	2.58			

Table S8: *Optical gap values (**Δo**) as calculated using TDDFT, evGW-BSE and qsGW-BSE in combination with the def2-TZVP basis sets. All values in eV. For $Si_{10}H_{16}$, for which the lowest excited state is not optically allowed, the gap towards the lowest bright excited state is given in between parentheses.*

Simulation details		TDDFT	evGW-BSE	qsGW-BSE
Nanoparticle	**Symmetry**	Δo	Δo	Δo
$Si_{10}H_{16}$	D_2	5.52 (5.79)	5.67 (5.92)	5.82 (6.13)
	T_d	5.64		
$Si_{35}H_{36}$	D_2	4.47	4.55	4.6
	T_d	4.47		
$Si_{84}H_{64}$	D_2	3.59		
	T_d	3.59		
$Si_{165}H_{100}$	D_2	3.05		
	T_d	3.05		

Table S9: *Fitting parameters obtained when fitting the Kohn-Sham HOMO-LUMO gap and the evGW fundamental gap data to the equation $\Delta_F = a + b/r^n$, where a is fixed, as discussed in the main text, to the bulk band-gap of silicon. DFT and evGW values were calculated using D2 symmetry and the basis-set shown in the table. Fitting parameters for the fundamental gap predictions from Reboredo et al.[1] from the literature are also included.*

Source	Method	Parameters		
		a	**b**	**n**
Original	**DFT, SVP**	1.1	9.84	0.57
	DFT, TZVP	1.1	9.02	0.52
	evGW, SVP	1.1	16.74	0.61
	evGW, TZVP	1.1	14.77	0.49
Reboredo	**Empirical pseudopotential**	1.1	35.29	1.37
		1.17	46.89	1.59

Table S10: *Fitting parameters obtained when fitting the optical gap data to the equation $\Delta_O = a + b/r^n$, where a is fixed, as discussed in the main text and equal to the bandgap of bulk silicon, 1.1 eV. TDDFT and evGW-BSE values were calculated using D2 symmetry and the def2-SVP basis-set. Fitting parameters b and n were fitted to data including the dark lowest energy excitation of $Si_{10}H_{16}$ (indicated by dark oscillator strength), and data including the lowest energy bright excitation (indicated by bright oscillator strength). The table also contains fitting parameters for fits to the optical gap data predicted by Wang et al.,*[2,3] *and Reboredo et al.,*[1] *plus the experimental (exp.) data of Wolkin et al.,*[4] *and Furukawa et al.,*[5] *is also included.*

Source	Methodology	Oscillator strength	Parameters		
			a	b	n
Original	TDDFT, SVP	Dark	1.1	8.61	0.59
		Bright	1.1	8.89	0.61
	TDDFT, TZVP	Dark	1.1	8.16	0.57
		Bright	1.1	8.62	0.59
	evGW-BSE, SVP	Dark	1.1	9.26	0.58
		Bright	1.1	9.85	0.62
	evGW-BSE, TZVP	Dark	1.1	6.85	0.41
		Bright	1.1	7.85	0.49
Wang	TB-TDDFT	--	1.1	9.51	0.69
Reboredo	Empirical pseudopotential	--	1.1	37.77	1.47
Wolkin	Experimental	--	1.1	22.94	1.28
Furukawa	Experimental		1.1	174.75	1.96

Table S11: *Fitting parameters obtained when fitting the exciton binding energy data to the equation $\Delta_O = a + b/r^n$, where a is equal to the exciton binding energy of bulk silicon, 0.014 eV. TDDFT and evGW-BSE values were calculated using D2 symmetry and the def2-SVP basis-set. Fitting parameters b and n were fitted to data including the lowest energy dark excitation of $Si_{10}H_{16}$ (indicated by dark oscillator strength), and data including the lowest energy bright excitation (indicated by bright oscillator strength).*

Method	Oscillator strength	Fitting constants	
		b	n
TDDFT	Dark	1.26	0.42
	Bright	0.69	0.17
evGW-BSE	Dark	7.47	0.63
	Bright	6.90	0.59

Table S12: *TDDFT predicted optical gap, photoluminescence energy and Stokes shift values, calculated using the def2-SVP basis-set, for the first four SiNPs. No symmetry constraint was applied when optimising the excited states, C1, to obtain the photoluminescence energies and Stokes shifts. All values in eV.*

Nanoparticle	Optical gap	Photoluminescence	Stokes Shift
$Si_{10}H_{16}$	5.73	0.80	4.93
$Si_{35}H_{36}$	4.49	2.89	1.60
$Si_{84}H_{64}$	3.69	3.19	0.50
$Si_{165}H_{100}$	3.15	2.91	0.24

Table S13: *TDDFT and evGW-BSE weighted contribution of the leading natural transition orbital (NTO) for the lowest lying excited state calculated using the def2-SVP basis set for the first four SiNPs studied.*

Nanoparticle	TDDFT NTO contribution	evGW-BSE NTO contribution
$Si_{10}H_{16}$	88.02%	69.94%
$Si_{35}H_{36}$	97.75%	84.01%
$Si_{84}H_{64}$	96.75%	69.71%
$Si_{165}H_{100}$	95.05%	75.46%

References

1 F. A. Reboredo, A. Franceschetti and A. Zunger, *Phys Rev B,* **61**, 13073-13086.

2 X. Wang, R. Q. Zhang, T. A. Niehaus, T. Frauenheim and S. T. Lee, *Journal of Physical Chemistry C*, 2007, **111**, 12588–12593.

3 X. Wang, R. Q. Zhang, S. T. Lee, T. A. Niehaus and T. Frauenheim, *Appl Phys Lett*, 2007, **90**, 123116.

4 M. V Wolkin, J. Jorne, P. M. Fauchet, G. Allan and C. Delerue, *Phys Rev Lett,* 1999, **82,** 197-200.

5 S. Furukawa and T. Miyasato, *Phys Rev B,* 1988, **38,** 5726-5729.