Supporting Information

Electronic Structure and Luminescence of 1.1 and 1.4 nm Silicon Nanocrystals: Oxide Shell versus Hydrogen Passivation

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Table S1 Caption

The radiative lifetime and oscillator strength of lowest transitions of species as described in the text. $Si_{66}O_{12}(OH)_{40}$ optimized at 3-21G level, with final energies calculated at 6-31G* level. Other species optimized at the 6-31G* level, with final energies calculated at cc-pVTZ(-f) level.

$Si_{35}H_{36}$				$Si_{66}H_{64}$			
Lowest Transitions **E** (eV)	Line Strength **S** (a.u.)	Oscillator Strength **f**	Radiative Lifetime τ (sec)	Lowest Transitions **E** (eV)	Line Strength **S** (a.u.)	Oscillator Strength **f**	Radiative Lifetime τ (sec)
5.00	0.17	0.00693	4.44E-08	4.24	0.09	0.003	1.45E-07
5.07	0.00	0.000	/	4.31	0.51	0.018	6.98E-08
5.11	3.15	0.131	6.75E-09	4.32	0.00	0.000	/
5.14	0.01	0.001	1.14E-06	4.39	0.29	0.010	1.14E-07
5.18	0.72	0.031	2.81E-08	4.40	0.00	0.000	3.25E-05
5.21	5.07	0.215	2.63E-09	4.48	1.26	0.046	1.67E-08
$Si_{29}O_6(OH)_{24}$				$Si_{66}O_{12}(OH)_{40}$			
Lowest Transitions **E** (eV)	Line Strength **S** (a.u.)	Oscillator Strength **f**	Radiative Lifetime τ (sec)	Lowest Transitions **E** (eV)	Line Strength **S** (a.u.)	Oscillator Strength **f**	Radiative Lifetime τ (sec)
2.88	0.01	0.001	3.98E-06	3.02	0.01	0.000	3.23E-06
2.88	0.03	0.002	1.24E-06	3.06	0.00	0.000	1.09E-04
3.00	0.00	0.000	2.79E-05	3.16	0.00	0.000	6.56E-06
3.46	0.04	0.003	5.64E-07	3.37	0.19	0.005	1.32E-07
3.47	0.03	0.003	7.13E-07	3.41	0.04	0.001	6.26E-07
3.58	0.00	0.000	/	3.44	0.02	0.001	1.11E-06
$Si_{35}(OH)_{36}$							
Lowest Transitions **E** (eV)	Line Strength **S** (a.u.)	Oscillator Strength **f**	Radiative Lifetime τ (sec)				
2.73	0.00	0.000	/				
2.87	0.00	0.000	/				
2.99	0.00	0.000	/				
3.74	0.08	0.002	6.90E-07				
3.88	0.00	0.000	/				
4.00	0.53	0.017	8.40E-08				

Table S2 Caption

The HOMO-LUMO gap comparison with different basis sets of structurally optimized species as described in the text. All energies in eV. $Si_{66}O_{12}(OH)_{40}$ optimized at 3-21G level. Other species optimized at the 6-31G* level.

Species	$Si_{35}H_{36}$		$Si_{29}O_6(OH)_{24}$		$Si_{35}(OH)_{36}$	
Basis Set	6-31G*	cc-pVTZ(-f)	6-31G*	cc-pVTZ(-f)	6-31G*	cc-pVTZ(-f)
HOMO	-6.67	-6.81	-5.45	-5.65	-5.49	-5.75
LUMO	-1.58	-1.81	-2.52	-2.77	-2.79	-3.03
Gap	5.09	5.00	2.93	2.88	2.69	2.73

Species	$Si_{66}H_{64}$		$Si_{66}O_{12}(OH)_{40}$
Basis Set	6-31G*	cc-pVTZ(-f)	6-31G*
HOMO	-6.37	-6.53	-5.56
LUMO	-1.86	-2.29	-2.54
Gap	4.51	4.24	3.02