Electronic supplementary information for

Density Functional Theory Study on the Surface Modification of Chlorine-Passivated Silicon Nanocrystals

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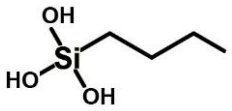
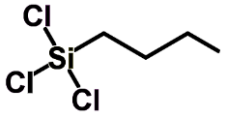
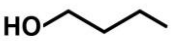
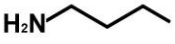
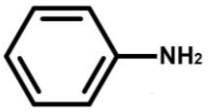
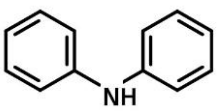
Table S1. Names and formulae of main organic molecules concerned in this work.

Name	molecular formula	structural formula
butyltrihydroxylsilane	$(HO)_3SiC_4H_9$	
n-butyltrichlorosilane	$C_4H_9Cl_3Si$	
butyllithium	C_4H_9Li	
1-butanol	$(HO)C_4H_9$	
butylamine	$(NH_2)C_4H_9$	
aniline	$(NH_2)C_6H_5$	
diphenylamine	$(NH)C_{12}H_{10}$	

Formation energy of a surface-modified Si NC

When the surface of a 0.8 nm fully Cl-passivated Si NC ($Si_{30}Cl_{39}$) is modified, all types of surface Si atoms (Si^A, Si^B and Si^C) are likely involved to form bonds with ligands. In the point of view of thermodynamics, the probability of the involvement of Si^A, Si^B or Si^C is related to the formation energy (E_f) of the surface-modified Si NC. E_f is obtained by using

$$E_f = E(Si_xCl_yC_zH_lN_mO_n) - x\mu(Si) - y\mu(Cl) - z\mu(C) - l\mu(H) - m\mu(N) - n\mu(O)$$

Where $E(Si_xCl_yC_zH_lN_mO_n)$ is the total energy of the surface-modifed Si NC at ground state at 0 K. *x*, *y*, *z, l, m* and *n* are the numbers of Si, Cl, C, H, N and O atoms, respectively. μ_{Si}, μ_{Cl}, μ_C, μ_H, μ_N, and μ_O, are the chemical potentials of Si, Cl, C, H, N and O respectively. The values of E_f are obtained by setting μ_{Si}, μ_{Cl}, μ_C, μ_H, μ_N, and μ_O equal to the total energy per atom of bulk Si (-7878.47 eV), the total energy per atom of chlorine gas (-12522.79 eV), the total energy per atom of diamond (-1036.88 eV), the total energy per atom of hydrogen gas (-15.88 eV), the total energy per atom of nitrogen gas (-1490.63 eV) and the total energy per atom of oxygen gas (-2046.11eV) at 0 K, respectively. Table S2 shows the E_f of the surface-modifed Si NC with a Si^A, Si^B or Si^C atom linked to a ligand, which is derived from a $(HO)_3$-Si-C_4H_9, C_4H_9Li, (OH)-C_4H_9 or (H_2N)-C_4H_9 molecule.

Table S2. Formation energies of silanized, alkylated, alkoxylated or aminized Si NCs. Butyltrihydroxylsilane (hydrolyzed n-butyltrichlorosilane), butyllithium, 1-butanol and butylamine are representatively used for the silanization, alkylation, alkoxylation and aminization of Si NCs, respectively. All types of surface Si atoms (Si^A, Si^B and Si^C) are likely involved to form bonds with ligands. There exists one ligand at the surface of each Si NC. The unit of formation energy is eV.

	silanization	**alkylation**	**alkoxylation**	**aminization**
Si^A	-222.23	-215.84	-209.97	-207.94
Si^B	-222.46	-215.80	-210.30	-208.27
Si^C	-222.59	-215.90	-210.35	-208.28