Supplementary Information (SI) for Dalton Transactions.

Supporting Information:

Data-driven Prediction of HSQ Polymer Structure and Silicon Nanocrystal Photoluminescence

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Experimental Methods

Materials

Trichlorosilane (Sigma Aldrich, 99%), methanol (Sigma Aldrich, anhydrous, 99.8%), ultra-high pure water, ethanol (200 proof, technical grade), hydrofluoric acid (Sigma Aldrich, ACS reagent, 48%), toluene (Fisher Chemical, Certified ACS), 1-dodecene (Sigma Aldrich, 95%), Sodium hydroxide (Fisher Chemical, Certified ACS). All chemicals were used as received, without further purification. Ultrapure Millipore water polished to a resistivity of 18.2 MΩ·cm was employed for all aqueous solutions.

Synthesis of polymer precursor from the trichlorosilane

For all polymer synthesis, varying mole ratios of trichlorosilane:water:methanol were employed. In a typical synthesis employing a 1:1:1 mole ratio, 30 mL of trichlorosilane was introduced into a round-bottom flask under an Ar atmosphere within an ice bath, equipped with an open outlet line submerged in NaOH solution. Subsequently, 13 mL of methanol was added to the flask. After a 20-minute reaction period, 5.4 mL water was swiftly introduced into the mixture and kept under Ar for 1 h. Given the substantial generation of HCl as a byproduct, it was imperative to maintain an open outlet line to avoid excessive pressure and mitigate the risk of flask rupture. The resulting white product underwent purification by successive washing with ethanol and deionized water until reaching a neutral pH of 7. Subsequently, the white powder was dried in the air at 80°C overnight to ensure complete desiccation.

Synthesis of the hydride terminated silicon nanocrystals

2 g of white polymer precursor was introduced into a tube furnace and subjected to a sequential heat treatment process under a forming gas (95% N_2/ 5% H_2). Initially, the precursor underwent heating at 600°C for a duration of 1 hour, followed by a subsequent treatment at 1100°C for an additional hour. The obtained product was ground in a mortar and pestle for 30 min until it became a fine powder. Subsequently, 300 mg of the fine powder was mixed with 10 mL of ethanol and 20 mL of hydrofluoric acid (HF), and the mixture was shielded from light for one hour to facilitate complete oxide etching and the liberation of hydride-terminated silicon nanocrystals*. Caution! HF is highly dangerous and should only be handled by personnel with extensive training.* Following the etching process, the solution was divided into multiple centrifuge tubes and extracted using toluene. After the initial centrifugation at 9500 rpm for 10 min, the etched sample was washed with an ethanol/toluene mixture three times and each time was centrifuged at 9500 rpm for 10 min to ensure complete removal of residual HF.

Surface functionalization of the hydride terminated silicon nanocrystals with 1-dodecene

Next, turbid and dark orange colored hydride terminated silicon nanocrystals were mixed with 10 mL of 1-dodecene and underwent three cycles of the pump-thaw-freeze process to remove the dissolved gases. Then, the reaction was performed at 190 °C under an Ar atmosphere in the Shlenk line overnight. A transparent solution was obtained and washed with a methanol/toluene mixture several times to remove unreacted 1-dodecene. The final precipitate was mixed with a small amount of toluene and filtered with a 0.45 µm PTFE syringe filter.

Table S1. Experimental details of fifteen silsesquioxane polymers

Sample mole ratios (HCl_3Si-H_2O-CH_3OH)	HCl_3Si (mL)	H_2O (mL)	CH_3OH (mL)	Reaction time	Etching time	Hydrosilylation time
1-1-0	30	5.4	0	1 hour	1 hour	Overnight (12-15 hours)
1-2-0	30	10.7	0			
1-3-0	30	16	0			
1-1-0.5	30	5.4	6			
1-2-0.5	30	10.7	6			
1-3-0.5	30	16	6			
1-1-1	30	5.4	13			
1-2-1	30	10.7	13			
1-3-1	30	16	23			
1-1-2	30	5.4	27			
1-2-2	30	10.7	27			
1-3-2	30	16	27			
1-1-3	30	5.4	41			
1-2-3	30	10.7	41			
1-3-3	30	16	41			

Sample Characterizations

X-ray Diffraction (XRD)

The crystallinity of alkyl-stabilized SiNCs was confirmed by X-ray diffraction using a Bruker-AXS APEX II diffractometer with Cu Kα radiation (λ = 1.54 Å). The generator current was set to 45 kV and 0.65 mA. Images of diffraction patterns were acquired for 13 min in the air. APEX II software was used to integrate the diffraction images from 8 to 60º, it was saved as a raw data and converted to .xy file.

Fourier-transform Infrared Spectroscopy (FTIR)

FTIR spectra of silsesquioxane polymers were collected with a Nicolet iS5 FTIR spectrometer equipped with an iD7 Attenuated Total Reflectance (ATR) accessory. For all measurements, the employed crystal was diamond and the angle of incidence was 45°. The acquired spectra were an average of 64 scans across the wavenumber range of 4000-400 cm^{-1} with a spectral resolution of 8 cm^{-1}. All FTIR data were baseline corrected using a spline curve.

Room Temperature Steady-state Photoluminescence

Steady-state photoluminescence of the alkyl-stabilized SiNCs spectra was acquired with an OceanOptics JAZ. The OceanOptics JAZ employed a 385 nm LED (ThorLabs; M385FP1) powered by a ThorLabs T-Cube LED driver (LEDD1B) as the excitation source which was coupled to OceanOptics UV-Visible optical fibers (QP400-2-UV-VIS or QP600-2-UV-VIS); the same fibers were employed for directing sample PL to the JAZ unit. All samples were collected with a 3 s integration time. All PL spectra were smoothed with a LOESS function (span of 0.1) due to the high level of noise introduced from the fiber-optic-based measurement.

Photoluminescent Quantum Yield

The PLQY ($\Phi_{PL)}$ of the alkyl-stabilized SiNCs was determined by collecting absorbance and photoluminescence spectra of SiNCs dispersed in toluene. Absorbance data for Table 2 PLQY calculation was collected with a Cary 100 Bio Double Beam UV-Vis Spectrophotometer, whereas for Fig. 5 PLQY calculation, the absorbance data was collected with 8453 UV-Vis spectrophotometer. The photoluminescence data was collected with a PerkinElmer LS 55 with an excitation wavelength of 421 nm and slit widths of 10 nm. PLQY was determined with the following equation, using coumarin 153 (Φ_{ref} = 0.54)[1] dissolved in ethanol as a reference fluorophore:

$$\Phi_{PL} = \Phi_{ref}(\frac{PL_{Si\,NC}}{PL_{Ref}})(\frac{Abs_{Ref}}{Abs_{Si\,NC}})(\frac{n^{2}_{Si\,NC}}{n^{2}_{Ref}})$$

where "Abs_{Ref}" is the absorbance value of reference at the excitation wavelength, "Abs_{SiNC}" is the absorbance value of the SiNC sample at the excitation wavelength, "PL_{Ref}" is the integrated photoluminescence emission spectrum area of the reference, "PL_{SiNC}" is the integrated photoluminescence emission spectrum area of a SiNC sample, and "n" is the refractive index of solvents used for dispersing reference (ethanol, 1.366) and sample (toluene, 1.496). All absorbance values were kept below 0.1 to minimize reabsorption.

Statistical Analysis

Response Surface Methodology

Response surface methodology (RSM) was performed with R code. For this study, molar ratios of trichlorosilane (X_1), water (X_2) and methanol (X_3) were chosen as independent variables. Percantages of cage in silsesquioxane polymers or PLQY values of alkyl-stabilized SiNCs were selected as a response (dependent) variable (Y). For the sake of simplicity, all molar ratios were coded to add up to 1 as given in Table S3.

A first order Scheffé's polynomial equation was used to fit the experimental results:

$$\hat{Y} = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3$$

where β_0, β_1, β_2, β_3 are fitting parameters. An analysis of variance (ANOVA) has been employed to determine the significance of the models.

Figures and Tables

The integrated FTIR absorption area ratios of Si-O-Si to Si-H

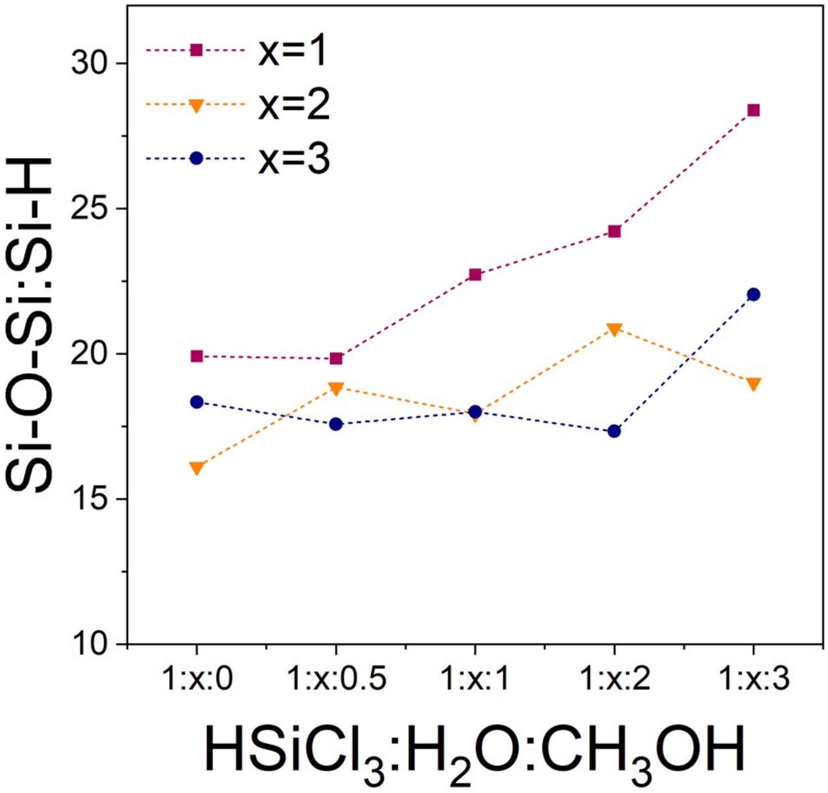

Fig. S1 The integrated FTIR absorption area ratios of Si-O-Si to Si-H, indicating the increase in the ratio as more methanol was added.

Gaussian fitting of Si-O-Si absorption peak

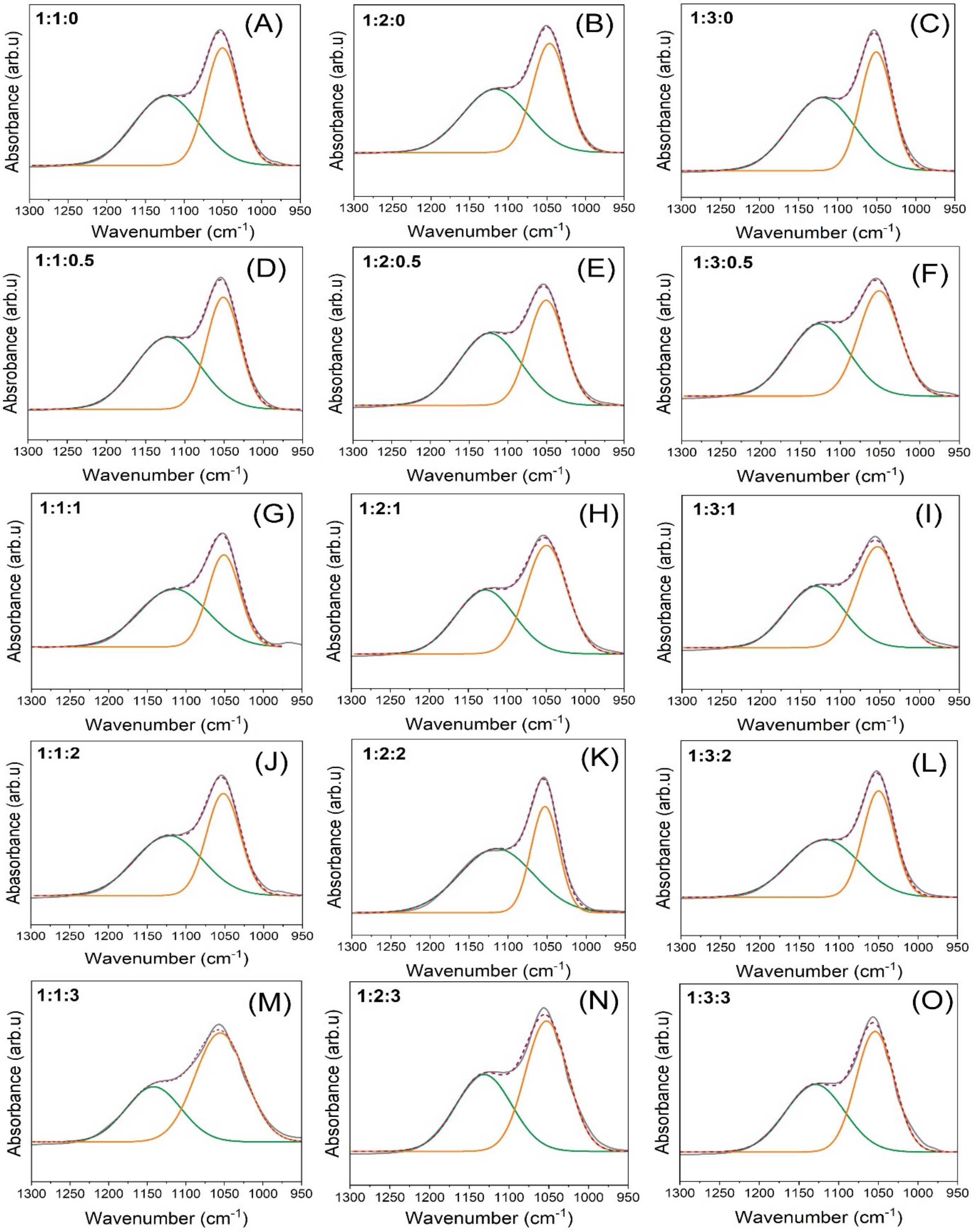

Fig. S2 Gaussian fitting of Si-O-Si absorption peak to determine cage and network % of 15 silsesquioxane polymers.

Deconvolution results of Si-O-Si peak

Table S2. The peak maxima of deconvolution and relative percentages of cage and network - structures for fifteen silsesquioxane polymers

Sample mole ratios ($HSiCl_3$-H_2O-CH_3OH)	Cage (cm^{-1})	Network (cm^{-1})	Cage (%)	Network (%)
1-1-0	1123	1050	52.9	47.1
1-2-0	1118	1046	52.5	47.5
1-3-0	1119	1050	55.6	44.4
1-1-0.5	1122	1051	55.4	44.6
1-2-0.5	1123	1050	53.6	46.4
1-3-0.5	1126	1050	50.8	49.2
1-1-1	1106	1050	57.2	42.8
1-2-1	1128	1049	45.6	54.4
1-3-1	1131	1052	45.5	54.5
1-1-2	1121	1051	53.7	46.3
1-2-2	1112	1052	61.1	38.9
1-3-2	1108	1049	54.2	45.8
1-1-3	1141	1055	39.4	60.6
1-2-3	1131	1052	43.8	56.2
1-3-3	1129	1054	45.6	54.4

Experimental and coded independent variables for RSM

Table S3. Experimental and coded independent variable data points for RSM modeling

Experimental molar ratios			**Coded molar ratios for RSM**		
$HSiCl_3$	**H_2O**	**CH_3OH**	**$HSiCl_3$**	**H_2O**	**CH_3OH**
1	1	0	0.500	0.500	0.000
1	2	0	0.333	0.667	0.000
1	3	0	0.250	0.750	0.000
1	1	0.5	0.400	0.400	0.200
1	2	0.5	0.286	0.571	0.143
1	3	0.5	0.222	0.667	0.111
1	1	1	0.333	0.333	0.333
1	2	1	0.250	0.500	0.250
1	3	1	0.200	0.600	0.200
1	1	2	0.250	0.250	0.500
1	2	2	0.200	0.400	0.400
1	3	2	0.167	0.500	0.333
1	1	3	0.200	0.200	0.600
1	2	3	0.167	0.333	0.500
1	3	3	0.143	0.429	0.429

Ternary plot for experimental molar ratio points

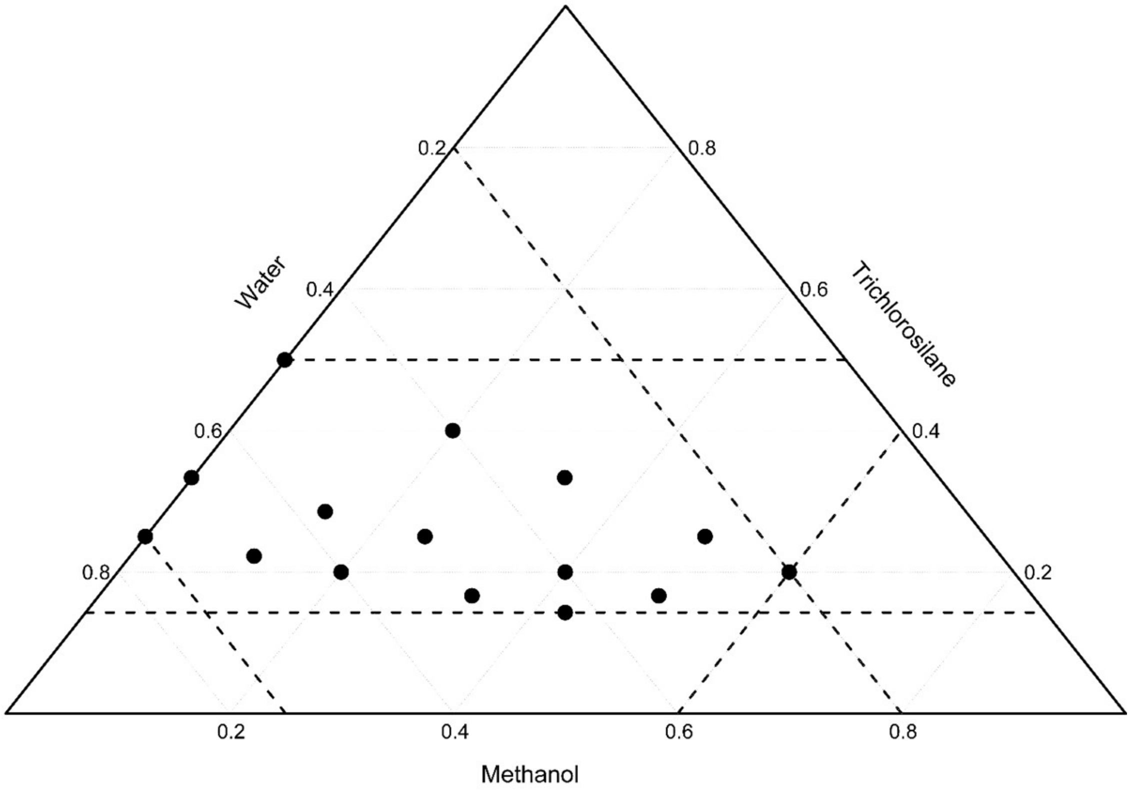

Fig. S3 Experimental molar ratio points mapped in the ternary plot with amount of each component in the reaction mixture varying from 0 to 1.

Table S4. Analysis of Variance (ANOVA) for prediction of cage percentages with 1st-order model.

Variable	DF	Sum of Squares	Mean Square	F value	p value
X_1(trichlorosilane)	1	35820	35820	1086.174	3.858×10^{-13}
X_2(water)	1	1904	1904	57.722	6.352×10^{-6}
X_3(methanol)	1	1611	1611	48.858	1.455×10^{-5}
Residuals	12	396	33		

Summary of RSM modeling residuals for cage percentages of 15 silsesquioxane polymers (1st order model)

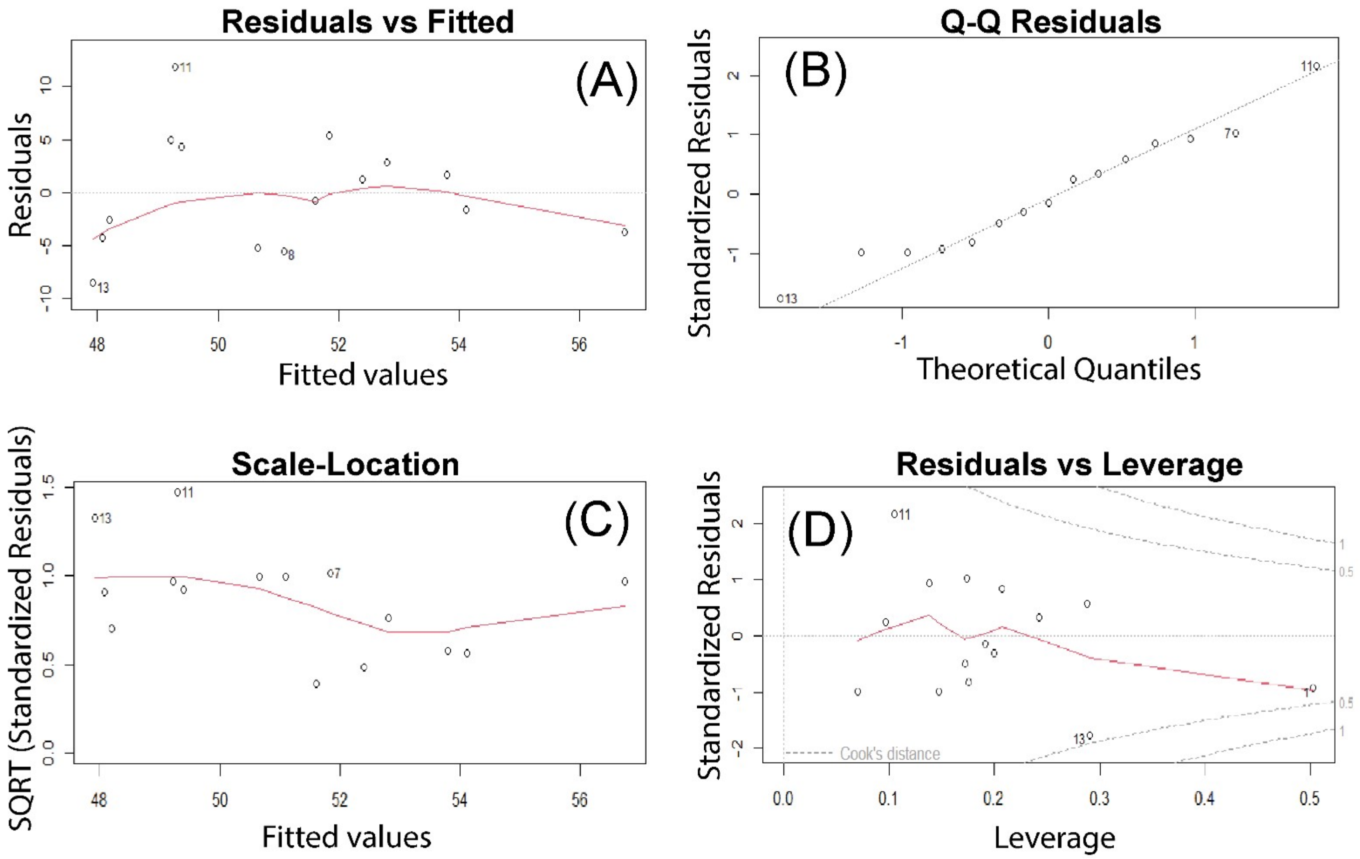

Fig. S4 The residual plots for RSM modeling of cage percentages of 15 silsesquioxane polymers. (A) Residuals of RSM model versus the fitted values, (B) Normal Q-Q Residuals, (C) Scale-Location, (D) Residuals versus Leverage plot

Table S5. Analysis of Variance (ANOVA) for prediction of cage percentages (inclusion of 2nd and 3rd order interactions)

Variable	DF	Sum of Squares	Mean Square	F value	p value
X_1(trichlorosilane)	1	35820	35820	992.8415	1.603×10^{-10}
X_2(water)	1	1904	1904	52.7620	4.746×10^{-5}
X_3(methanol)	1	1611	1611	44.6600	9.029×10^{-5}
X_1 X_2(trichlorosilane: water)	1	59	59	1.6315	0.2335
X_1 X_3(trichlorosilane: methanol)	1	11	11	0.3016	0.5963
X_1 X_2 X_3 (trichlorosilane: water: methanol)	1	1	1	0.0358	0.8542
Residuals	9	325	36		

Table S6. Analysis of Variance (ANOVA) for prediction of PLQY (%) with 1st-order model.

Variable	DF	Sum of Squares	Mean Square	F value	p value
X_1(trichlorosilane)	1	457.23	457.23	84.5187	8.816×10^{-7}
X_2(water)	1	34.00	34.00	6.2853	0.02756
X_3(methanol)	1	50.29	50.29	9.2967	0.01010
Residuals	12	64.92	5.41		

Table S7. Analysis of Variance (ANOVA) for prediction of PLQY (%) (inclusion of 2nd and 3rd order interactions)

Variable	DF	Sum of Squares	Mean Square	F value	p value
X_1(trichlorosilane)	1	457.23	457.23	90.2256	5.481×10^{-6}
X_2(water)	1	34.00	34.00	6.7097	0.02920
X_3(methanol)	1	50.29	50.29	9.9244	0.01173
X_1 X_2(trichlorosilane: water)	1	15.21	15.21	3.0016	0.11722
X_1 X_3(trichlorosilane: methanol)	1	2.91	2.91	0.5751	0.46762
X_1 X_2 X_3 (trichlorosilane: water: methanol)	1	1.18	1.18	0.2336	0.64043
Residuals	9	45.61	5.07		

Summary of RSM modeling residuals for the relative PLQY values of SiNCs with 1^{st}-order model

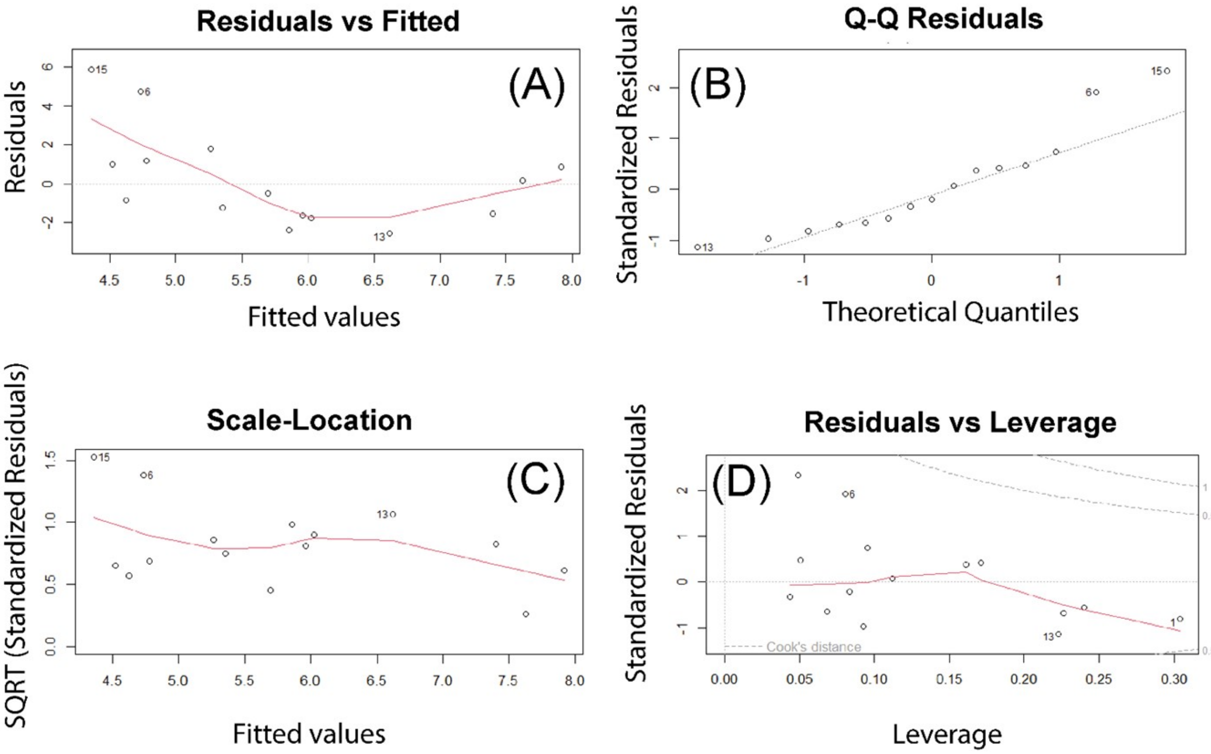

Fig. S5 The fitting parameters for RSM modeling of the relative PLQY values of SiNCs derived from 15 silsesquioxane polymers. (A) Residuals of RSM model versus the fitted values, (B) Normal Q-Q Residuals, (C) Scale-Location, (D) Residuals versus Leverage plot

Validation of RSM model-FTIR

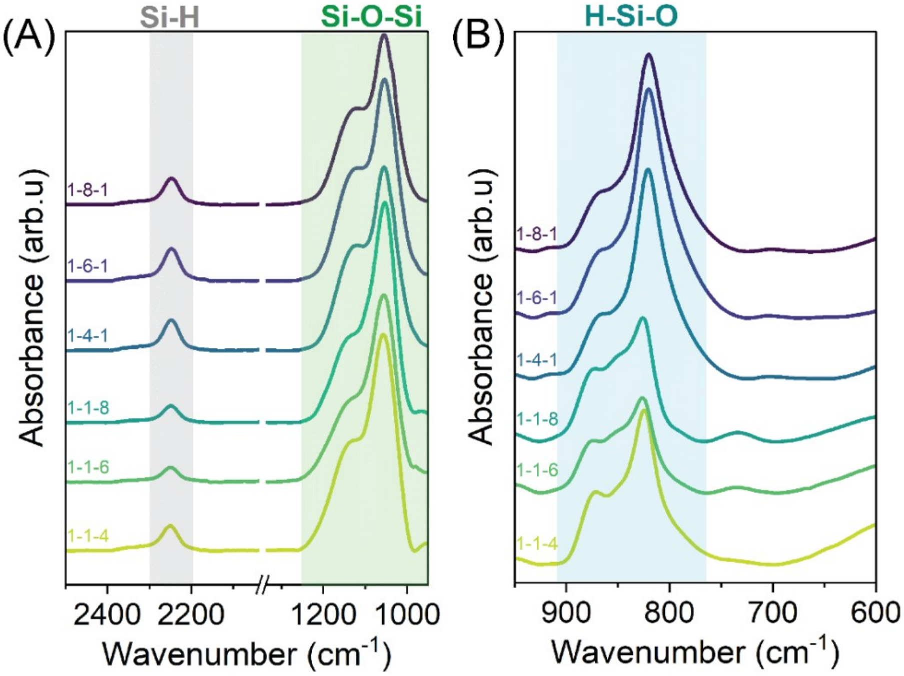

Fig. S6 FTIR spectra of silsesquioxane polymers prepared with various molar ratios of trichlorosilane, water and methanol to validate the RSM model. (A) FTIR spectra for wavenumber in between 2500 and 950 cm^{-1}, highlighting Si-H and Si-O-Si stretching vibrations. (B) FTIR spectra for wavenumber in between 950 and 600 cm^{-1}, showing H-Si-O bending vibrations which indicates a small shift for peak absorption of network type structure from 818 to 824 cm^{-1}.

Validation of RSM model- Gaussian fitting of Si-O-Si absorption peak

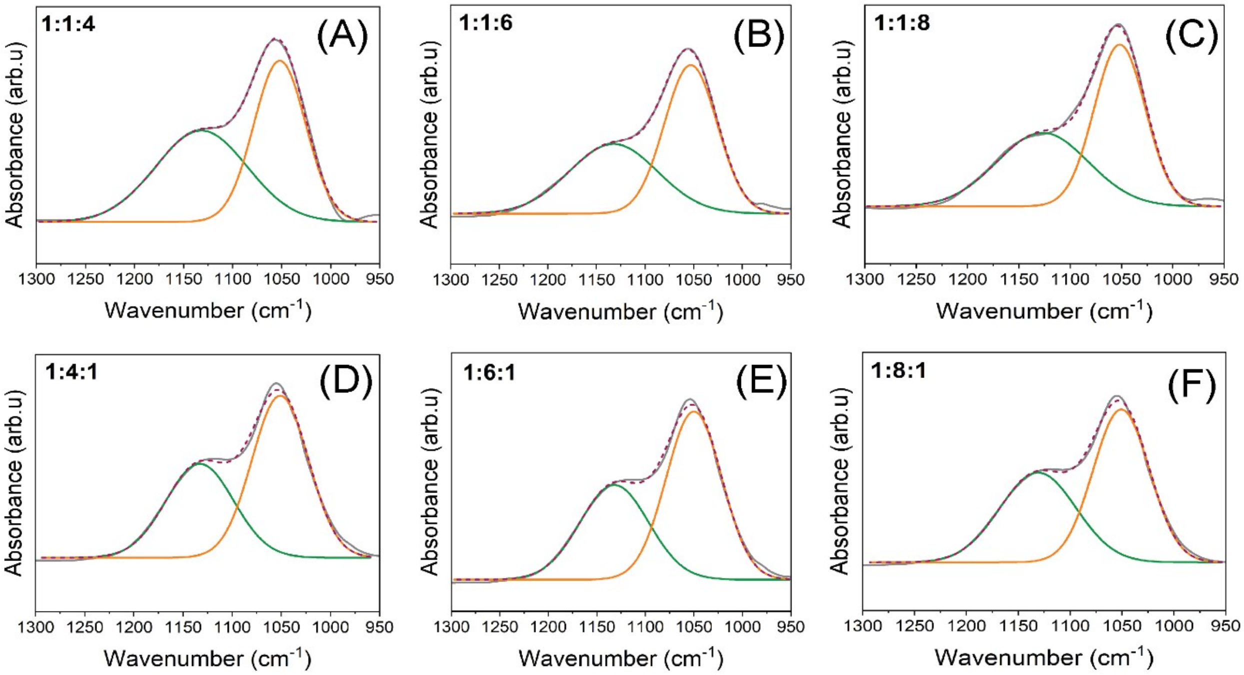

Fig. S7 Gaussian fitting of Si-O-Si absorption peak to determine cage and network % of silsesquioxane polymers which was synthesized to validate RSM models.

Validation of RSM model- XRD and PL of alkyl-stabilized SiNCs

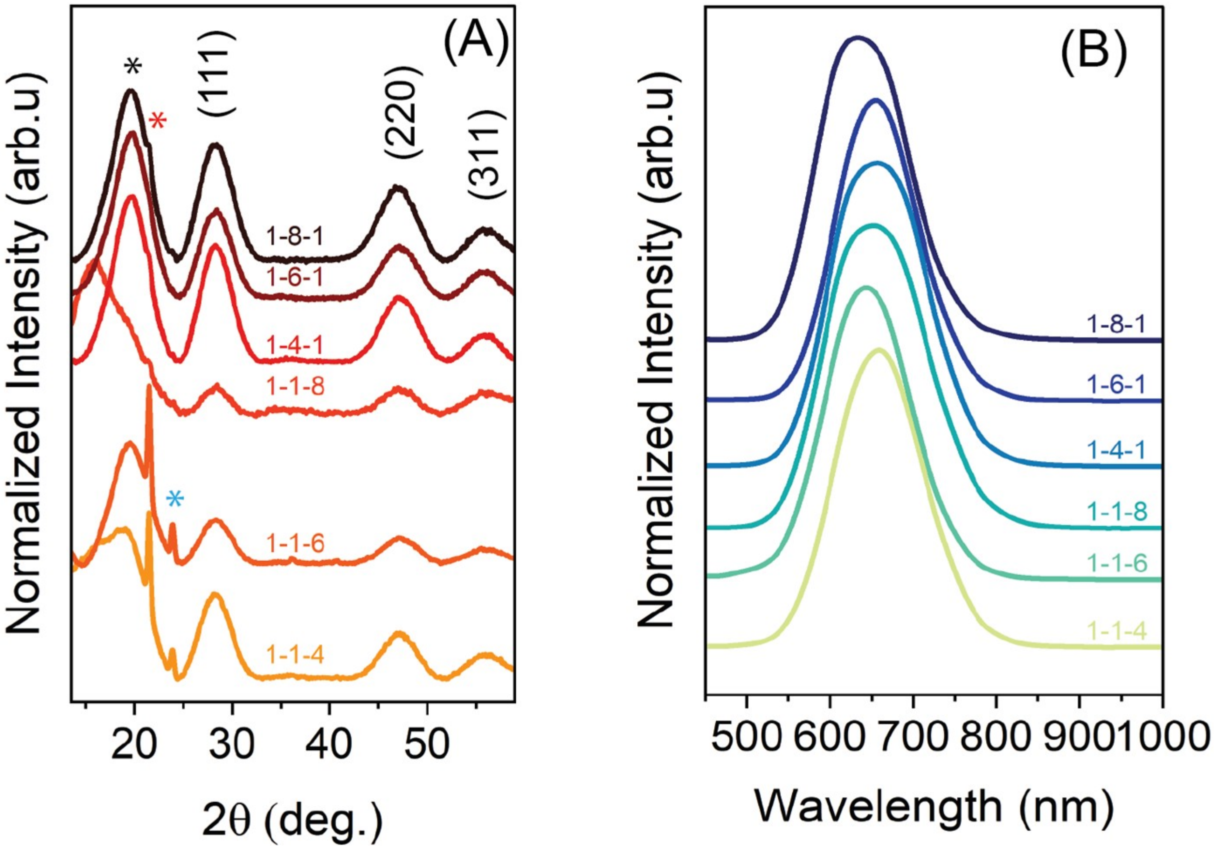

Fig. S8 (A) XRD patterns of alkyl-stabilized Si nanocrystals synthesized from silsesquioxane polymers used to validate the RSM model. A broad feature near 19.5° (black asterisk) is attributed to amorphous SiO_2, while a sharper peaks at ~21.5° (red asterisk) and peak at 23.8° (blue asterisk) correspond to crystalline SiO_2.[2,3] An additional broad feature near 15° for sample 1-1-8 may be associated with impurities from the etching or sample preparation (B) PL spectra of alkyl-stabilized SiNCs .

Validation of RSM model- PL properties and XRD crystallite sizes of alkyl-stabilized SiNCs

Table S8. PL properties and XRD crystallite sizes of alkyl-stabilized SiNCs for validation of RSM model

Sample Mole ratios (HCl_3Si-H_2O-CH_3OH)	PL peak maximum (nm)	FWHM (nm)	Crystallite size from XRD (nm)
1-1-4	659	124	2.1
1-1-6	645	120	1.8
1-1-8	655	137	2.5
1-4-1	658	131	2
1-6-1	657	115	2.2
1-8-1	640	124	2.1

References:

1 K. Rurack and M. Spieles, *Anal Chem*, 2011, 83, 1232–1242.

2 R. T. Downs and D. C. Palmer, *American Mineralogist*, 1994, 79, 9–14.

3 W. A. Dollase and W. H. Baur, *American Mineralogist*, 1976, 61, 971–978.