

Supplementary material (ESI) for the Journal of Materials Chemistry

**Biocompatible and Stable ZnO Quantum Dots
Generated by Functionalization with Siloxane-core
PAMAM Dendrimers**

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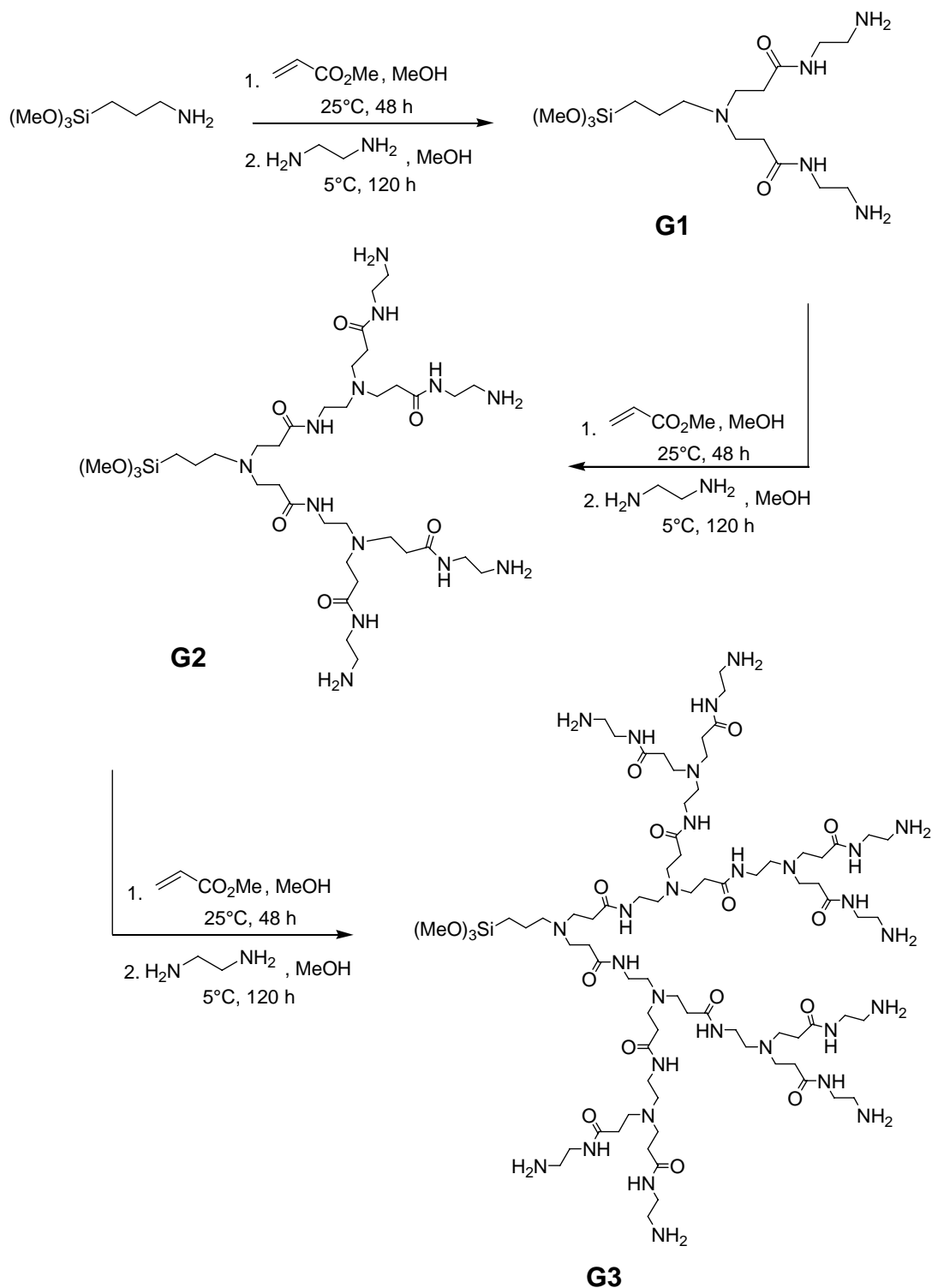
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1. Syntheses and products studies

1.1. Synthesis of siloxane-core PAMAM dendrimers

Six novel dendrons bearing a siloxane group at the focal point have been prepared from 3-aminopropyltrimethoxysilane, methyl acrylate and ethylene diamine (Scheme 1).



Scheme S1. Synthetic route to siloxane-core PAMAM dendrimers

The synthesis of siloxane-core PAMAM dendrons was performed according to Tomalia *et al.*¹ with slight modifications.

1.1.1. Synthesis of G0.5 dendron

Under nitrogen flow, to a mixture of 3-aminopropyltrimethoxysilane (2 g, 11 mmol) and 20 mL of MeOH was added dropwise at room temperature methyl acrylate (17.2 g, 200 mmol). After 48 h stirring at rt, the solution was heated at 40°C for 30 min. After cooling at rt, MeOH and methyl acrylate were evaporated. The product was obtained as a colorless liquid in 97% yield.

¹H NMR (DMSO-d₆, 200 MHz) : δ = 3.55 (s, 6H, COOCH₃); 3.44 (s, 9H, Si(OCH₃)₃); 2.62 (t, J = 6.6 Hz, 4H, CH₂CH₂COOCH₃); 2.46-2.22 (m, 6H, CH₂COOCH₃ + SiCH₂CH₂N); 1.48-1.27 (m, 2H, SiCH₂CH₂CH₂); 0.50 (t, J = 8.1 Hz, 2H, SiCH₂).

¹³C NMR (DMSO-d₆, 50 MHz) : δ = 172.1, 55.7, 51.1, 49.9, 48.8, 32.0, 19.9, 5.9.

1.1.2. Synthesis of G1.0 dendron

Under nitrogen flow, to a mixture of ethylene diamine (69.4 g, 1.14 mol) and methanol (17 mL) cooled to 4°C, was added dropwise a 50 weight % solution of dendron G0.5 (4g, 11.4 mmol) in 5 mL MeOH. The mixture was stirred at 4°C for 4 days and then finally heated to 40°C for 30 min. remaining ethylene diamine was removed by azeotrope using a 3/1 toluene/MeOH mixture.

The product was obtained as a pale yellow liquid in 95% yield.

¹H NMR (DMSO-d₆, 200 MHz) : δ = 7.95 (s broad, 2H, CONH); 3.42 (s, 9H, Si(OCH₃)₃); 3.09-2.88 (td, J = J' = 4.6 Hz, 4H, CONHCH₂); 2.72-2.35 (m, 14H, CH₂NH₂); 1.51-1.42 (m, 2H, SiCH₂CH₂CH₂); 0.49 (t broad, 2H, SiCH₂).

¹³C NMR (DMSO-d₆, 50 MHz) : δ = 171.8, 55.7, 49.9, 49.5, 42.4, 41.5, 33.3, 19.9, 7.7.

HRMS (ESI): m/z calculated for C₁₆H₃₇N₅O₅Si [M+H]⁺, 407.26; found, 407.2.

1.1.3. Synthesis of G1.5 dendron

The synthesis was conducted as described for G0.5 dendron but using 4.9 mmol of the G1 dendron and 39.2 mmol methyl acrylate in 4.5 mL MeOH. The product was obtained as a viscous pale yellow oil in quantitative yield.

¹H NMR (DMSO-d₆, 200 MHz) : δ = 7.63 (s large, 2H, CONH); 3.55 (s, 12H, COOCH₃); 3.41 (s, 9H, Si(OCH₃)₃); 3.21-2.93 (m, 4H, CONHCH₂); 2.71-2.23 (m, 26H, CH₂NH₂); 1.48-1.32 (m, 2H, SiCH₂CH₂CH₂); 0.49 (t large, 2H, SiCH₂).

¹³C NMR (DMSO-d₆, 50 MHz) : δ = 172.6, 171.4, 54.9, 52.4, 51.3, 49.8, 49.3, 49.0, 48.7, 36.8, 32.1, 20.0, 9.2.

1.1.4. Synthesis of G2.0 dendron

The synthesis was conducted as described for G1.0 dendron but using 5.1 mmol of the G1.5 dendron and 1.88 mol ethylene diamine in 125 mL MeOH. The product was obtained as a viscous pale yellow oil in a quantitative yield.

¹H NMR (DMSO-d₆, 200 MHz): δ = 8.01 (s broad, 2H, CONH); 7.91 (t broad, 2H, CONH); 3.35 (s large, 9H, Si(OCH₃)₃); 3.21-2.94 (m, 12H, CONHCH₂); 2.72-2.05 (m, 38H, CH₂NH₂); 1.48-1.34 (m, 2H, SiCH₂CH₂CH₂); 0.50 (t broad, 2H, SiCH₂).

¹ D. A. Tomalia, B. Huang, D. R. Swanson, H. M. Brothers II and J. W. Klimash, *Tetrahedron* 2003, **59**, 3799.

¹³C NMR (DMSO-d₆, 50 MHz): δ = 171.7, 171.6, 52.4, 51.1, 50.5, 49.8, 45.1, 42.4, 42.1, 41.5, 34.6, 33.4, 19.8, 10.7.

HRMS (ESI): m/z calculated for C₃₆H₇₇N₁₃O₉Si [M+H]⁺, 863.57; found, 863.1.

1.1.5. Synthesis of G2.5 dendron

The synthesis was conducted as described for G0.5 dendron but using 2.32 mmol of the G1 dendron and 37.5 mmol methyl acrylate in 4.0 mL MeOH. The product was obtained as a viscous pale yellow oil in a quantitative yield.

¹H NMR (DMSO, 200 MHz): δ = 7.96 (t broad, 2H, CONH); 7.65 (t broad, 4H, CONH); 3.56 (s, 24H, COOCH₃); 3.34 (s, 9H, Si(OCH₃)₃); 3.23-2.91 (m, 12H, CONHCH₂); 2.83-2.08 (m, 70H); 1.50-1.33 (m, 2H, SiCH₂CH₂CH₂); 0.51 (t broad, 2H, SiCH₂).

¹³C NMR (DMSO, 50 MHz): δ = 172.6, 171.3, 55.6, 52.7, 51.4, 51.3, 49.8, 49.7, 49.3, 49.2, 49.0, 48.9, 36.7, 34.6, 33.3, 32.1. Signals for Si-CH₂ and Si-CH₂-CH₂ could not be assigned due to their low intensity.

1.1.6. Synthesis of G3 dendron

The synthesis was conducted as described for G1.0 dendron but using 2.58 mmol of the G1.5 dendron and 3.63 mol ethylene diamine in 241 mL MeOH. The product was obtained as a viscous pale yellow oil in a quantitative yield.

¹H NMR (DMSO-d₆, 200 MHz): δ = 8.76 (t broad, 2H, CONH); 8.05 (t broad, 2H, CONH); 3.49 (s broad, 9H, Si(OCH₃)₃); 3.44-2.40 (m, 114H); 1.49-1.33 (m, 2H, SiCH₂CH₂CH₂). Signal for Si-CH₂ could not be assigned due to its low intensity.

¹³C NMR (DMSO-d₆, 50 MHz): δ = 171.6, 171.5, 52.4, 51.1, 50.0, 49.9, 49.8, 49.7, 49.6, 45.0, 44.2, 42.3, 41.4, 37.0, 36.0, 34.4, 33.4, 30.9, 21.1. Signal for Si-CH₂ could not be assigned due to its low intensity.

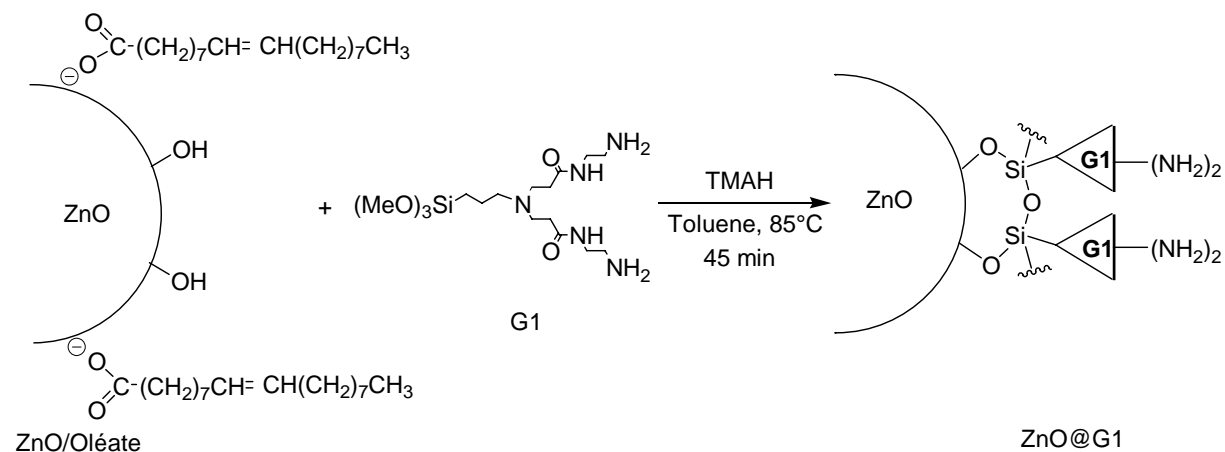
HRMS (ESI): m/z calculated for C₇₆H₁₅₇N₂₉O₁₇Si [M+H]⁺, 1776.21; found, 1776.7.

1.2. Functionalization of oleate-capped ZnO nanoparticles with siloxane-core PAMAM dendrons

1.2.1. Synthesis of oleate-capped ZnO QDs

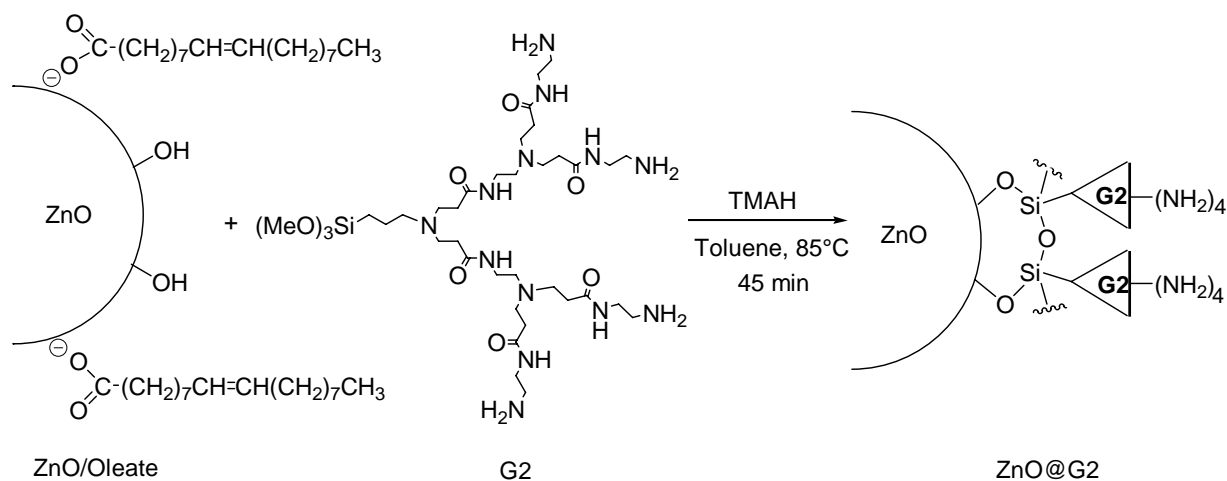
Zinc acetate (220 mg, 1.2 mmol) was dissolved in hot ethanol (20 mL) under vigorous stirring. Oleic acid (70 mL, 0.22 mmol) is then added and the mixture is heated to reflux. In a separate flask, tetramethylammonium hydroxide (360 mg, 1.99 mmol) is dissolved in refluxing ethanol (5 mL). This solution is then rapidly injected in the flask containing $\text{Zn}(\text{OAc})_2$ and oleic acid and the mixture was refluxed for 2 min. The mixture is then diluted with EtOH (50 mL) and cooled down to 0°C with an ice-bath. A white precipitate of ZnO nanoparticles appeared. Particles were centrifuged (15 min at 4000 rpm) with removal of the supernatant. The resulting oleate-capped ZnO QDs were washed several times with ethanol, in which they are insoluble, and finally suspended in toluene (10 mL). Oleate capped ZnO QDs were stored at 4°C in the dark.

1.2.2. Synthesis of ZnO@G1 QDs



Under a nitrogen atmosphere, the oleate-capped ZnO QDs previously prepared were dispersed in 10 mL toluene and treated with 1 mL of a 0.1 M solution of G1 dendron in EtOH. After 5 min stirring at room temperature, 1 mL of a 0.3 M solution of tetramethylammonium hydroxide (TMAH) in EtOH is injected and the temperature was set at 85°C. After 45 min, the solution was allowed to cool and nanoparticles isolated by centrifugation (4000 rpm, 15 min). After removal of the supernatant, ZnO@G1 QDs were washed three times with toluene in which they are insoluble. QDs were then redispersed in water and were further purified by successive precipitation-solubilization rounds using acetone as bad-solvent. After drying for 5 h *in vacuo*, QDs were redispersed in water for further experiments.

1.2.3. Synthesis of ZnO@G2 QDs



ZnO@G2 nanoparticles were prepared analogously to the reaction above, with the exception that 1 mL of a 0.6 M TMAH solution in EtOH was added to the oleate-capped ZnO QDs and to the G2 dendron.

1.3. Characterization of nanoparticles

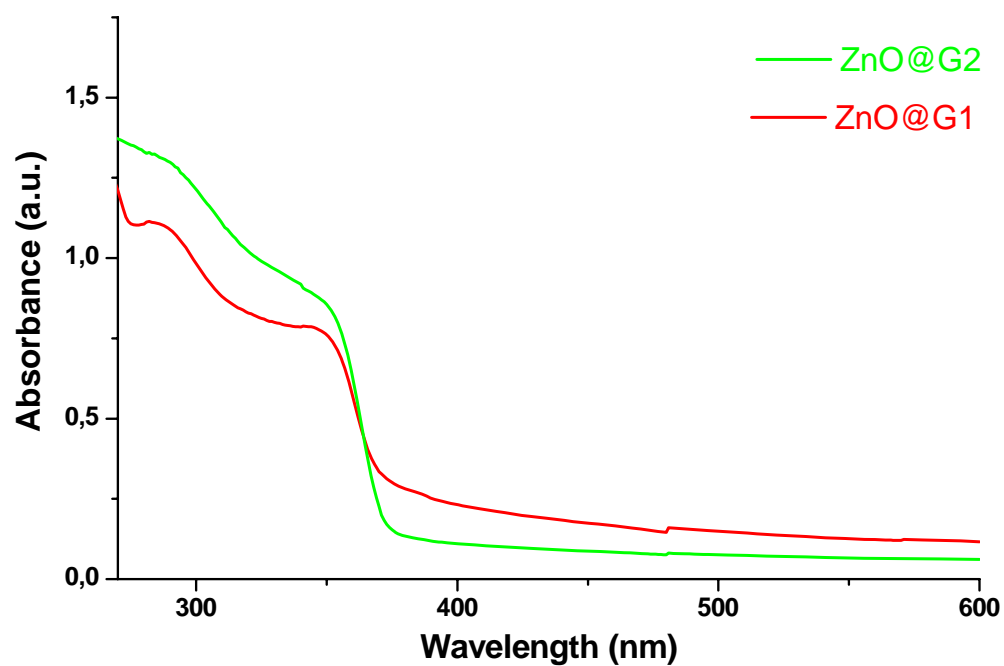


Figure S1. Room temperature absorption of ZnO@G1 and ZnO@G2 QDs dispersed in water.

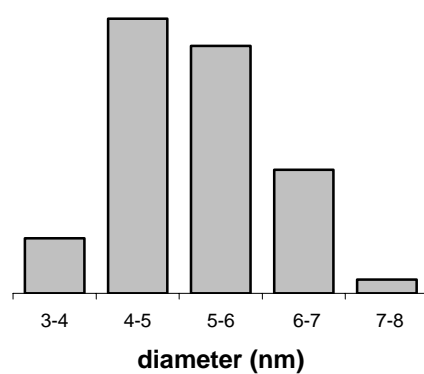
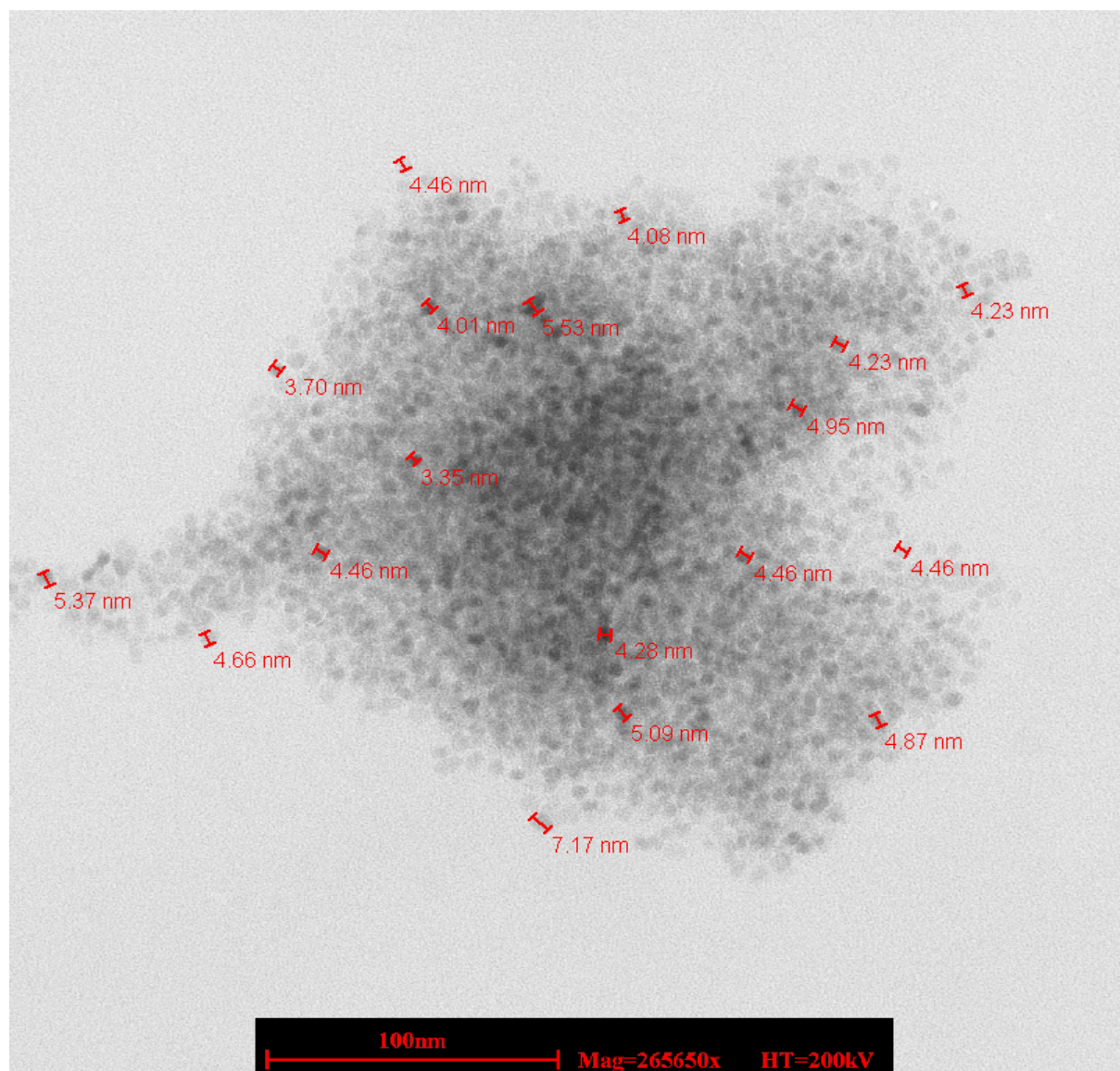


Figure S2. TEM image of water-soluble ZnO@G1 QDs and the corresponding size distribution. The average diameter of QDs (ca. 100 particles counted) is 5.3 nm.

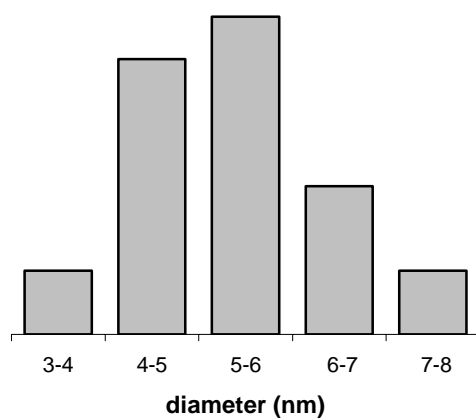
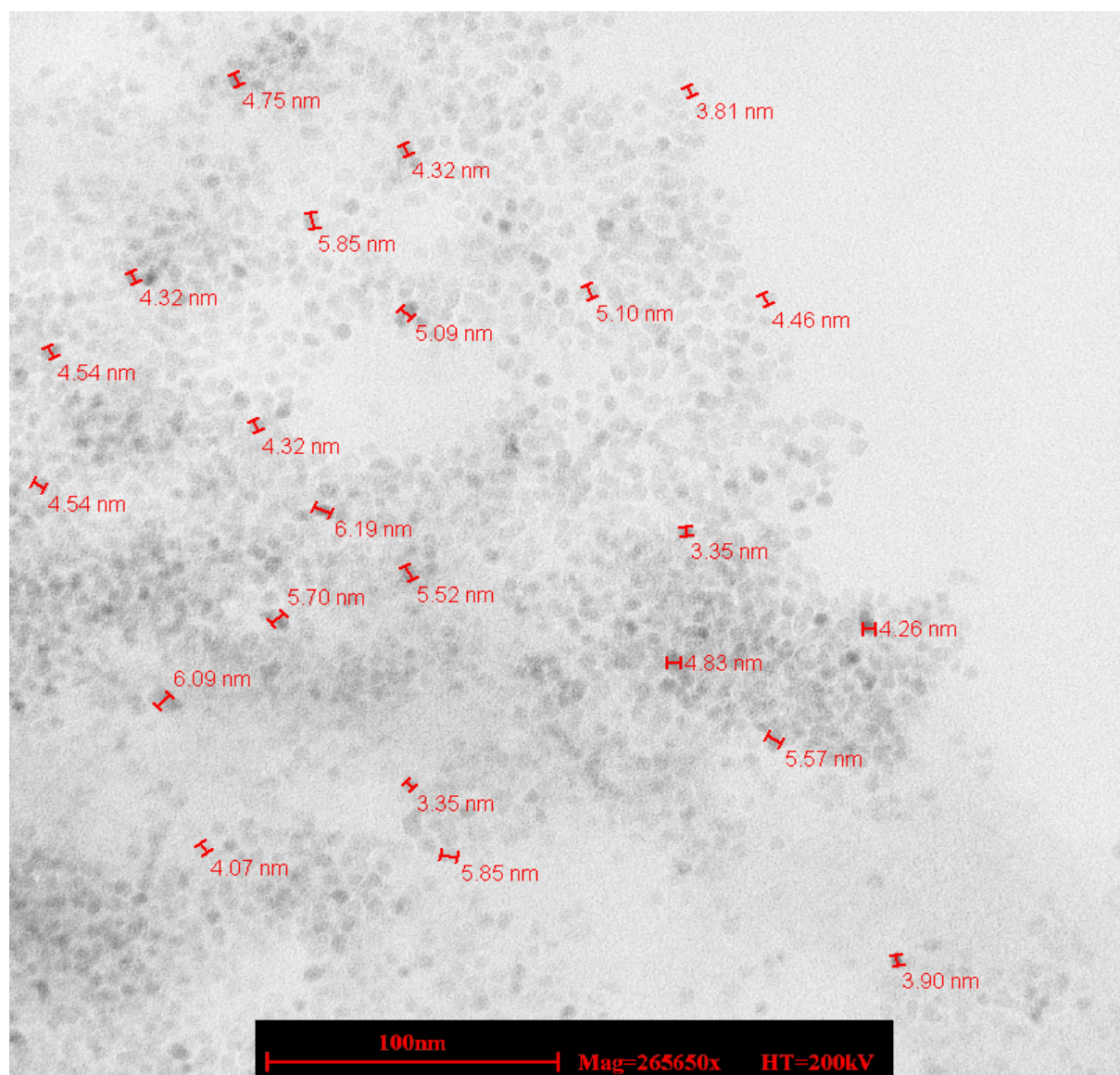


Figure S3. TEM image of water-soluble ZnO@G2 QDs and the corresponding size distribution. The average diameter of QDs (ca. 100 particles counted) is 5.1 nm.

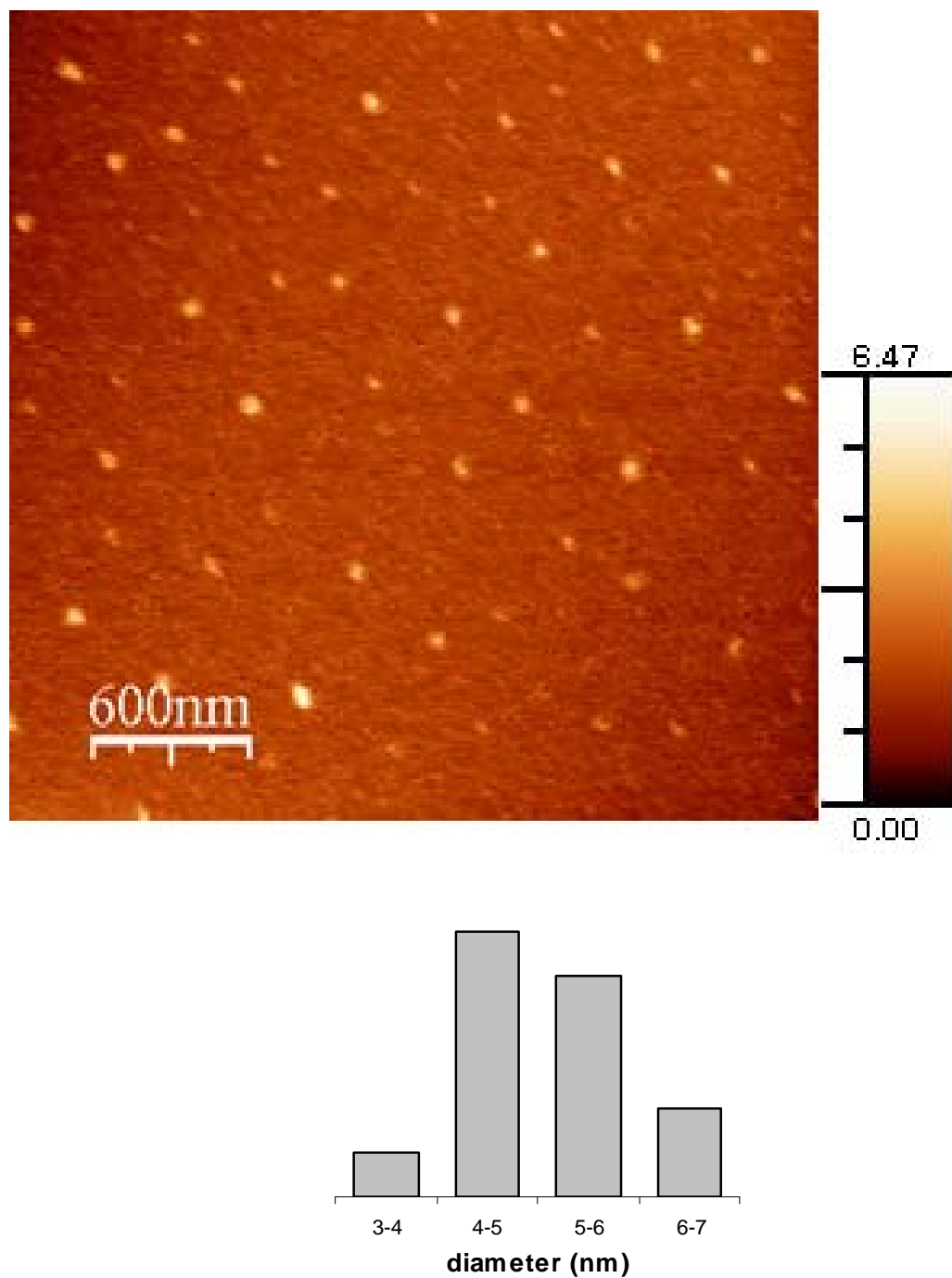


Figure S4. AFM image of water-soluble ZnO@G1 QDs and the corresponding size distribution determined using AFM heights. The average diameter of QDs is 4.9 nm.

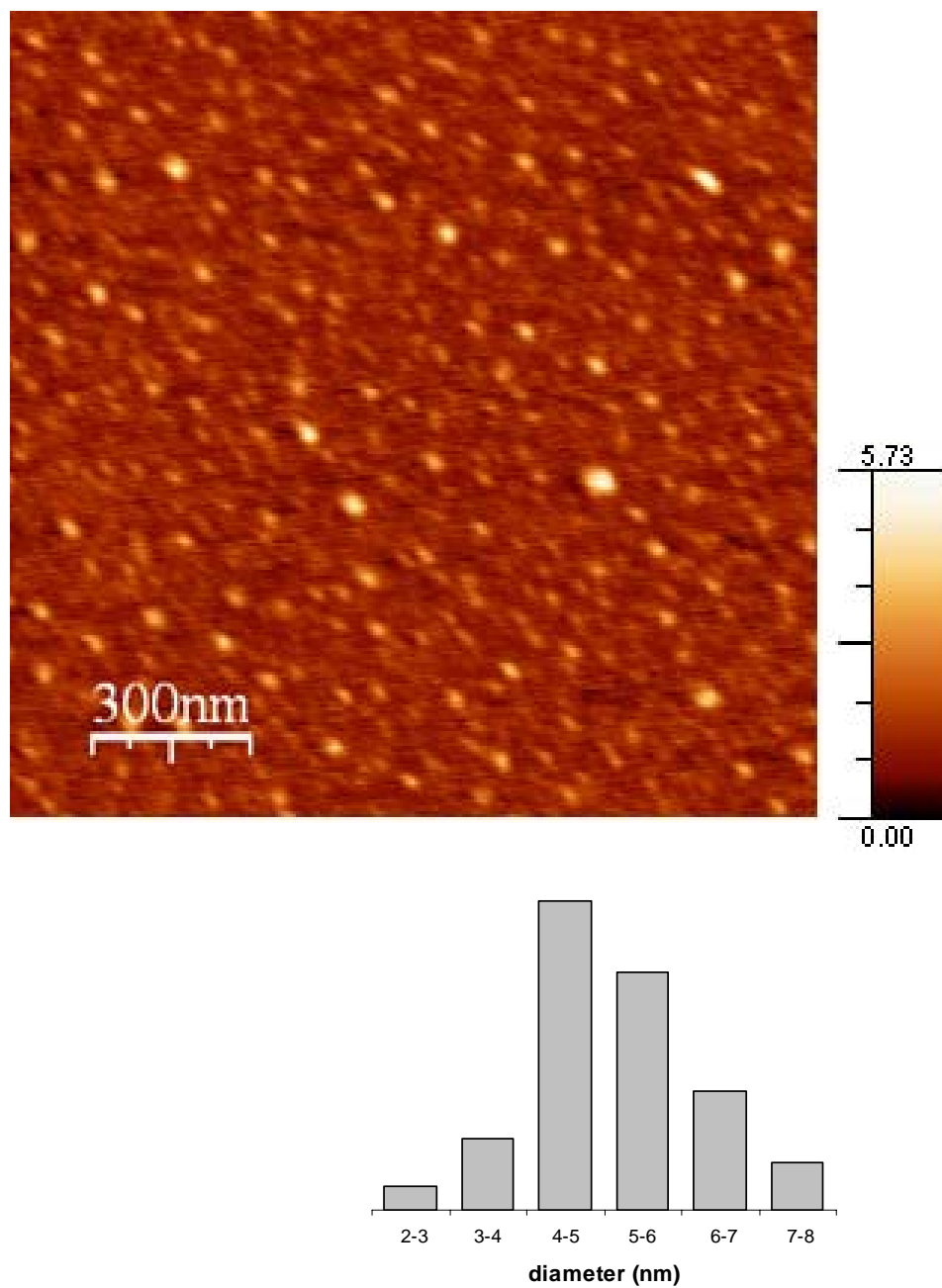


Figure S5. AFM image of water-soluble ZnO@G2 QDs and the corresponding size distribution determined using AFM heights. The average diameter of QDs is 4.6 nm.

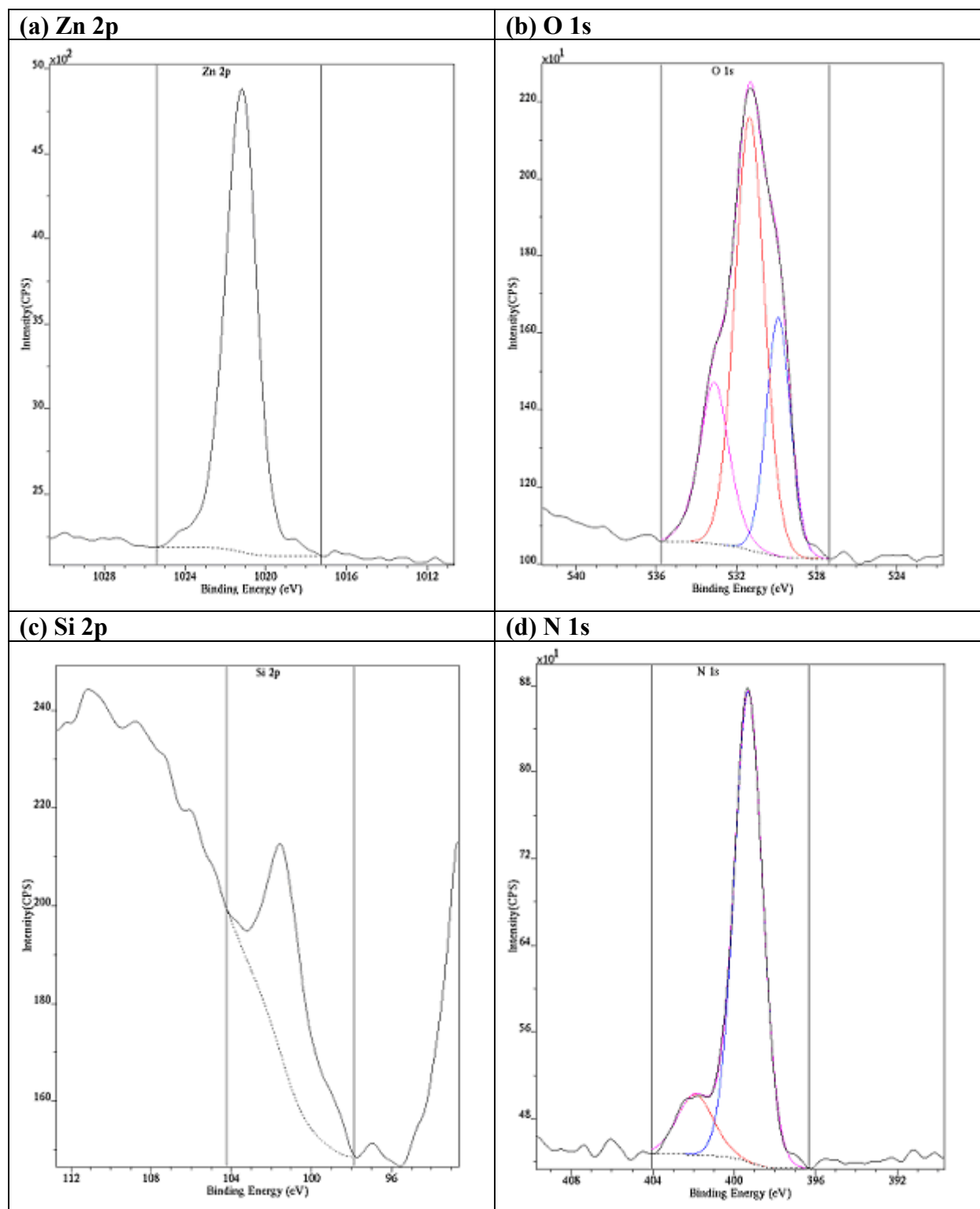


Figure S6. Zn 2p (a), O 1s (b), Si 2p (c) and N 1s (d) X-ray photoelectron spectra of ZnO@G2 QDs.

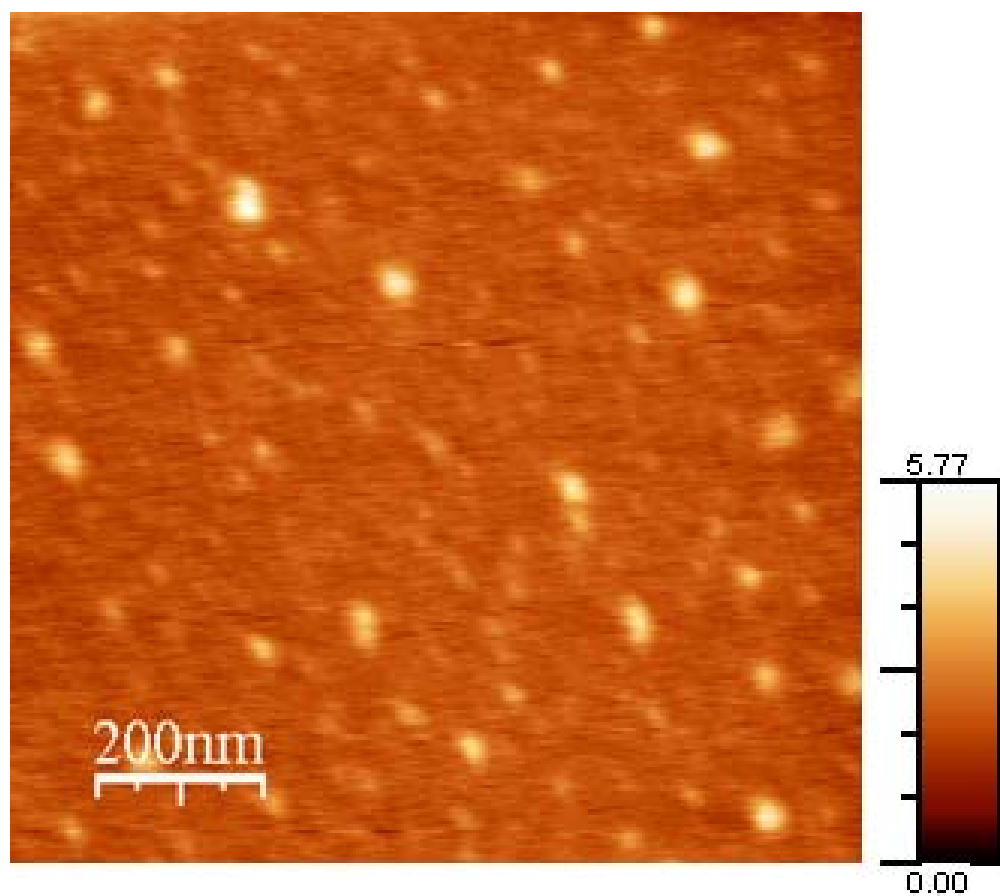


Figure S7. AFM image of the ZnO-G3 nanocomposite. The average diameter of QDs is 5.2 nm.

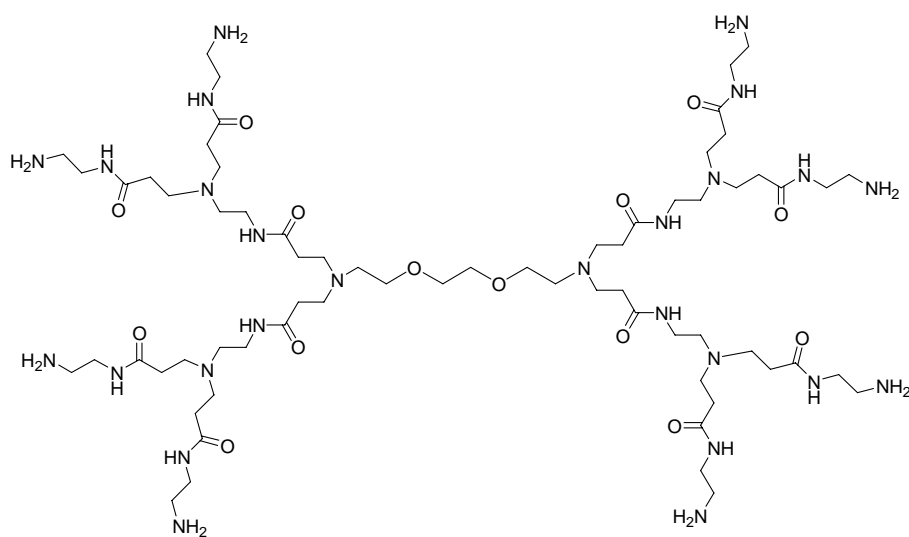


Figure S8. Chemical structure of the G2 dendrimer bearing no siloxane unit at the focal point.

2. Confocal imaging experiments

Mag	Zoom	ΔZ
60.16	4.4	288 nm

	Width	Height
Resolution	512 pixels	512 pixels
Pixel size	87nm	87 nm
Box size	44.56 μm	44.56 μm

(a)

λ (580-over nm)

(b)

λ (530-560 nm)

Figure S9. Confocal microscopy images of *S. aureus* cells labeled with ZnO@G2 QDs (a) red fluorescence (over 580 nm), and (b) green fluorescence (530-560 nm). The mean surfaces ($0.5 \pm 0.16 \mu\text{m}^2$) and the circularity (0.92 ± 0.06) of fluorescent objects determined by laser scanning microscopy are in good accordance with those of *S. aureus* cells. Image width and height are equal to $44.6 \mu\text{m}$ (pixel size 87 nm) and analysed depth = $0.3 \mu\text{m}$.