Supplementary Information (SI) for Nanoscale Advances.

Supplementary materials

Ligand-engineered ZnS quantum dots synthesized from substituted thioureas: scalable production, polymer grafting, and emissive film fabrication

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Synthesis of disubstituted thioureas

Typical procedure for isothiocyanate synthesis

Substituted isothiocyanates were synthesized according to a previously reported procedure [1]. Briefly, potassium carbonate (K_2CO_3, 0.055 mol) was dissolved in 30 ml of distilled water, and the corresponding amine (0.050 mol) was added under vigorous stirring at room temperature. Carbon disulfide (CS_2, 0.10 mol) was then added dropwise, and the reaction mixture was stirred for 3 h. After cooling the mixture in an ice bath (0-5 °C), a solution of trichlorotriazine (TCT, 0.025 mol) in 20 ml of dichloromethane (DCM) was added dropwise with continuous stirring. A white precipitate formed during the addition. After 1 h of stirring, 10% aqueous NaOH was added dropwise until the pH exceeded 11, resulting in complete dissolution of the precipitate. The aqueous layer was extracted with DCM, and the combined organic layers were washed with 1% aqueous HCl and brine, then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography (petroleum ether : DCM = 9:1).

Benzyl isothiocyanate

Colorless oil, yield: 78%.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ 7.35-7.38 (m, 2H), 7.32-7.33 (d, *J* = 7.05 Hz, 1H), 7.28-7.30 (m, 2H), 4.67 (s, 2H). ^{13}C NMR (125.76 MHz, CDCl3): δ 134.21 (NCS); 129.03; 128.43; 126.90; 48.70.

Octyl isothiocyanate

Colorless oil, yield: 83%.
^{1}H NMR (500.13 MHz, CDCl$_3$): δ 3.51 (t, *J* = 6.70 Hz, 2H), 1.67-1.73 (m, 2H), 1.38-1.44 (m, 2H), 1.27-1.32 (m, 16H), 0.89 (t, *J* = 6.91 Hz, 3H).
^{13}C NMR (125.76 MHz, CDCl$_3$): δ 129.45 (NCS); 45.13; 31.99; 30.05; 29.69; 29.59; 29.48; 29.42; 28.89; 26.63; 22.77; 14.20.

Oleyl isothiocyanate

Colorless oil, yield: 72%.
^{1}H NMR (500.13 MHz, CDCl$_3$): δ 5.27-5.37 (m, 2H), 3.34-3.36 (m, 2H), 1.98-2.03 (m, 2H), 1.62-1.69 (m, 2H), 1.39-1.45 (m, 2H), 1.25-1.30 (m, 22H), 0.85-0.89 (t, 3H). ^{13}C NMR (125.76 MHz, CDCl$_3$): δ 155.9 (NCS); 130.0; 129.7; 41.50; 32.0; 29.8-29.1 (multiple CH$_2$); 27.3; 26.3; 22.7; 14.2.

Typical procedure for the preparation of di- and trisubstituted thioureas

A dry benzene (or dichloromethane) (75 ml) solution of the corresponding isothiocyanate (0.05 mol) was prepared, and the appropriate amine (0.055 mol) was added in one portion under continuous stirring at ambient temperature. The reaction mixture was stirred for several hours, and the progress was monitored by thin-layer chromatography (TLC). Upon completion, the crude product was passed through a short silica gel plug to remove residual reagents. The solvent was evaporated under reduced pressure using a rotary evaporator, affording the desired thiourea, which was used without further purification.

Characterization of substituted thioureas (TU1-TU11)

1-allyl-3-octylthiourea (TU1)

Yellow oil, quantitative yield. ^{1}H NMR (500.13 MHz, CDCl$_3$): δ (br.s, 2NH), 5.82-5.75 (m, 1H), 5.19-5.08 (dd, *J* = 27.44, 17.78 Hz, 2H), 4.02 (s, 2H), 3.36 (s, 2H), 1.51-1.48 (m, 2H), 1.32-1.21 (m, 10H), 0.80 (t, *J* = 6.83 Hz, 1H).
^{13}C NMR (125.76 MHz, CDCl$_3$): δ 181.62(C=S); 133.59; 116.93; 46.82; 44.65; 31.40; 28.93; 26.54; 25.41; 22.49; 22.02; 13.96.

N-allylpiperidine-1-carbothioamide (TU2)

Yellow oil, quantitative yield. ^{1}H NMR (500.13 MHz, CDCl$_3$): δ 5.83-5.79 (m, 1H), 5.64 (br.s, NH), 5.10-5.01 (dd, *J* = 28.76, 15.48 Hz, 2H), 4.19 (s, 2H), 3.67 (s, 4H), 1.53 (s, 2H), 1.49 (s, 4H).
^{13}C NMR (125.76 MHz, CDCl$_3$): δ 180.89 (C=S); 134.30; 116.67; 116.65; 48.86; 48.42; 25.36; 24.16.

1-Octyl-3-phenylthiourea (TU3)

White semisolid, quantitative yield. ^{1}H NMR (500.13 MHz, CDCl$_3$): δ 8.35 (br.s, NH), 7.42 (t, *J* = 7.70 Hz, 2H), 7.29 (t, *J* = 7.70 Hz, 1H), 7.21-7.23 (d, *J* = 7.86 Hz, 2H), 6.06 (br.s, NH), 3.58-3.62 (m, 2H), 1.52-1.58 (m, 2H), 1.24-1.29 (m, 10H), 0.87 (t, *J* = 6.86 Hz, 3H).

^{13}C NMR (125.76 MHz, $CDCl_3$): δ 180.34 (C=S), 130.26; 127.23; 125.26; 45.60; 31.82; 29.36; 29.02; 26.94; 22.70; 14.19.

N-phenylmorpholine-4-carbothioamide (TU4)

White solid, yield: 94 %. ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.52 (s, NH), 7.32 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.11-7.13 (d, *J* = 7.77, 2H), 3.76-3.78 (m, 4H), 3.67-3.69 (m, 4H).
^{13}C NMR (100.61 MHz, $CDCl_3$): 183.6 (C=S)l; 140.0; 129.3; 125.5; 123.4; 66.2; 49.7.

(Z)-N-(Octadec-9-enyl)-N'-phenylthiourea (TU5)

White semisolid, yield: 96%. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 8.52 (s, NH), 7.40 (t, *J* = 7.86 Hz, 2H), 7.20-7.28 (m, 3H), 6.07 (s, NH), 5.31-5.37 (m, 2H), 3.56-3.61 (m, 2H), 1.95-2.02 (m, 4H), 1.50-1.57 (m, 2H), 1.23-1.33 (m, 22H), 0.86 (t, *J* = 6.74 Hz, 3H).
^{13}C NMR (125.76 MHz, $CDCl_3$): δ 180.3; 136.5; 129.1; 128.3; 127.1; 125.2; 45.5; 29.8; 27.3; 22.8; 14.2.

1-dodecyl-3-octylthiourea (TU6)

White semisolid, quantitative yield. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 5.81 (br.s, 2NH), 3.31 (s, 4H), 1.54-1.48 (m, 4H), 1.26-1.17 (m, 28H), 0.79 (t, *J* = 7.24 Hz, 6H).
^{13}C NMR (125.76 MHz, $CDCl_3$): δ 181.20 (C=S); 44.41; 31.82; 31.69; 29.56; 29.54; 29.50; 29.44; 29.26; 29.21; 29.16; 29.09; 28.94; 26.84; 22.60; 22.55; 14.04; 14.00.

N-dodecylpiperidine-1-carbothioamide (TU7)

White-off semisolid, quantitative yield. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 5.41 (br.s, NH), 3.68 (t, *J* = 4.60 Hz, 4H), 3.57-3.53 (q, *J* = 13.44, 6.91 Hz, 2H), 1.58-1.50 (m, 8H), 1.22-1.16 (m, 18H), 0.79 (t, *J* = 6.95 Hz, 1H).
^{13}C NMR (125.76 MHz, $CDCl_3$): δ 181.09 (C=S); 48.61; 46.22; 31.82; 29.56; 29.54; 29.50; 29.47; 29.30; 29.25; 26.94; 25.33; 24.20; 22.60; 14.04.

1-benzyl-3-allylthiourea (TU8)

White powder, quantitative yield. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 7.27-7.20 (m, 5H), 6.40 (br.s, NH), 6.24 (br.s, NH), 5.76-5.68 (m, 1H), 5.09-5.05 (m, 2H), 4.56 (s, 2H), 3.94 (s, 2H).
^{13}C NMR (125.76 MHz, $CDCl_3$): δ 181.95 (C=S); 136.88; 133.07; 128.80; 127.88; 127.50; 117.23; 48.49; 46.73.

N-benzylmorpholine-4-carbothioamide (TU9)

White-off powder, quantitative yield. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 7.29-7.22 (m, 5H), 5.73 (br.s, 1NH), 4.78-4.77 (d, *J* = 4.89 Hz, 2H), 3.71-3.62 (dt, *J* = 43.34, 27.81, 4.69 Hz, 8H).
^{13}C NMR (125.76 MHz, $CDCl_3$): δ 182.56 (C=S); 137.64; 128.76; 128.03; 127.77; 66.05; 50.24; 47.49.

1,3-Dioctylthiourea (TU10)

Yellow semisolid, quantitative yield.
^{1}H NMR (500.13 MHz, $CDCl_3$): δ 5.99 (br.s, NH, 2H), 3.39 (m, 2H), 1.55-1.61 (m, 4H), 1.25-1.34 (m, 20H), 0.86 (t, *J* = 6.86 Hz, 6H).
^{13}C NMR (125.76 MHz, $CDCl_3$): δ 181.37 (C=S); 31.86; 29.34; 29.28; 27.02; 22.72; 14.17.

3-allyl-1,1-diethylthiourea (TU11)

Yellow oil, quantitative yield. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 5.89-5.84 (m, 1H), 5.35 (br.s, NH), 5.13-5.05 (dd, *J* = 26.16, 13.55 Hz, 2H), 4.26-4.22 (td, *J* = 11.11, 4.83, 1.53 Hz, 2H), 3.60-3.55 (q, *J* = 14.21, 7.10 Hz, 4H), 1.14 (t, *J* = 7.18 Hz, 6H).
^{13}C NMR (125.76 MHz, $CDCl_3$): δ 180.16 (C=S); 134.33; 116.66; 48.39; 45.08; 12.58.

Characterization of ZnS QDs prepared from substituted thioureas (TU1-TU11)

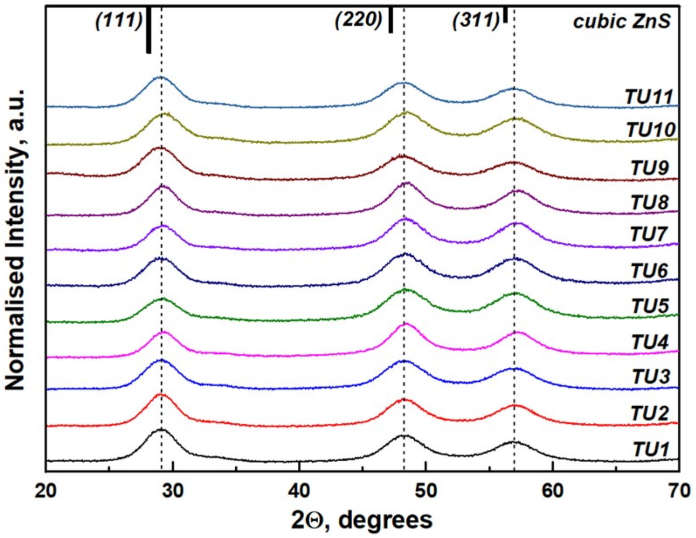
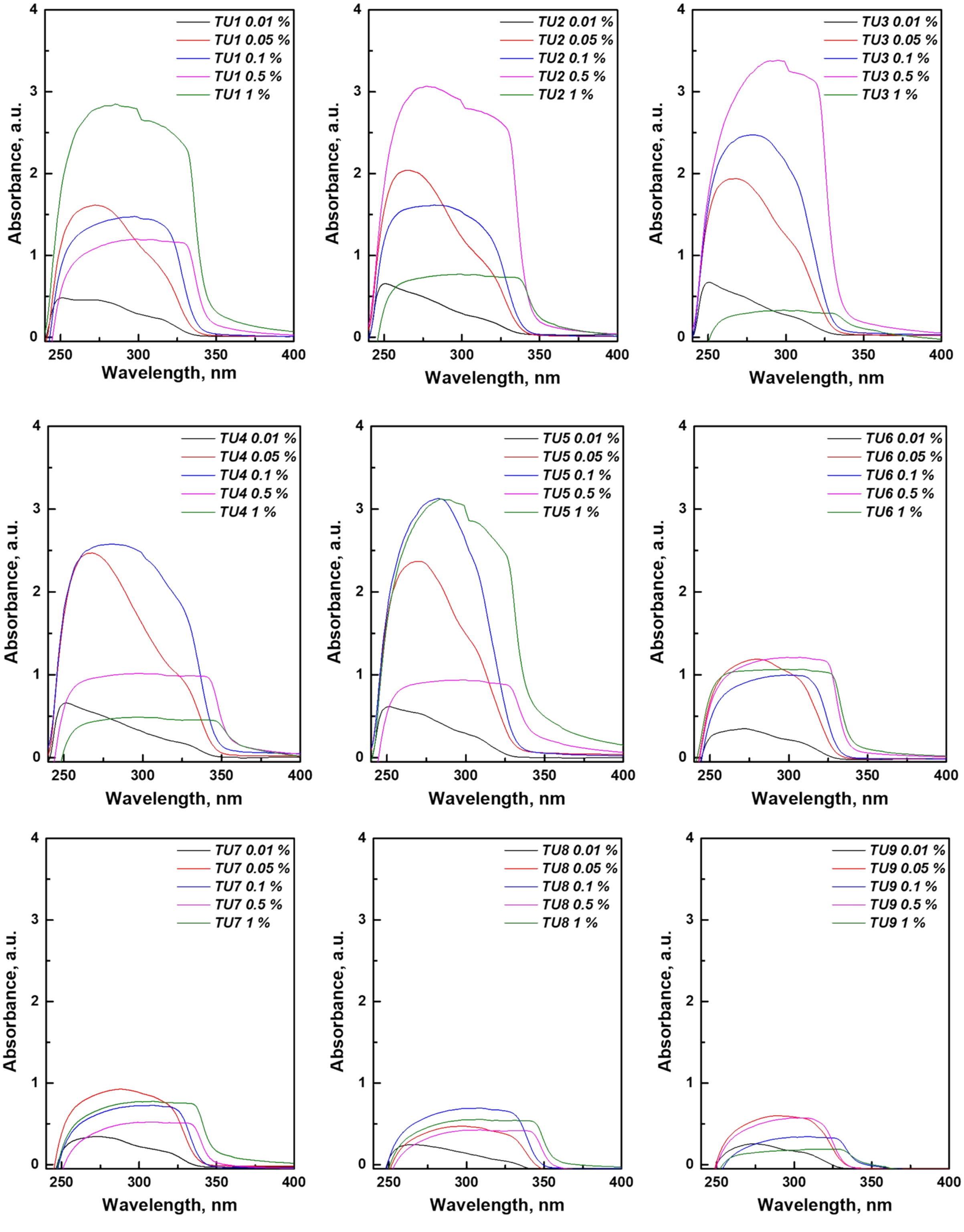


Figure S1. XRD patterns of ZnS QDs synthesized by the hot-injection method from various substituted thioureas.

Table S1. Lattice parameters of ZnS QDs prepared from various substituted thioureas and ZnS QDs synthesized from **TU5** with different capping ligands.

TU	Lattice parameter a, Å
TU1	5.433
TU2	5.467
TU4	5.444
TU5	5.427
TU6	5.508
TU7	5.455
TU8	5.458
TU5 Large-Scale	5.510

Ligand	Lattice parameter a, Å
LA (TU5)	5.510
2-MPA	5.365
BMEP	5.349
PODM	5.404


TU1 0.01 %
TU1 0.05 %
TU1 0.1 %
TU1 0.5 %
TU1 1 %
TU2 0.01 %
TU2 0.05 %
TU2 0.1 %
TU2 0.5 %
TU2 1 %
TU3 0.01 %
TU3 0.05 %
TU3 0.1 %
TU3 0.5 %
TU3 1 %
TU4 0.01 %
TU4 0.05 %
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TU4 1 %
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TU8 0.5 %
TU8 1 %
TU9 0.01 %
TU9 0.05 %
TU9 0.1 %
TU9 0.5 %
TU9 1 %
Absorbance, a.u.
0
1
2
3
4
Wavelength, nm
250
300
350
400

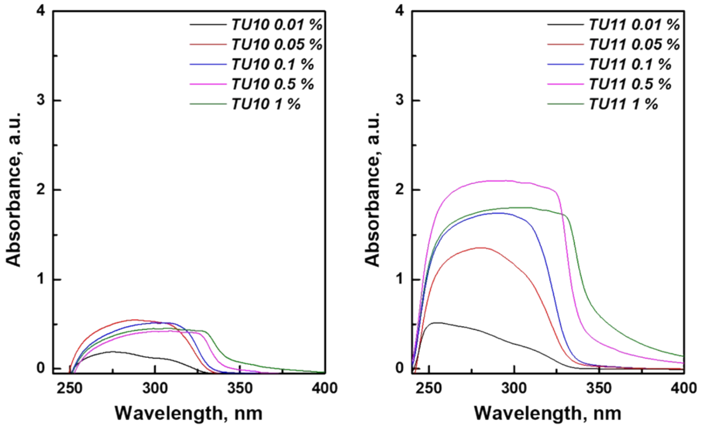
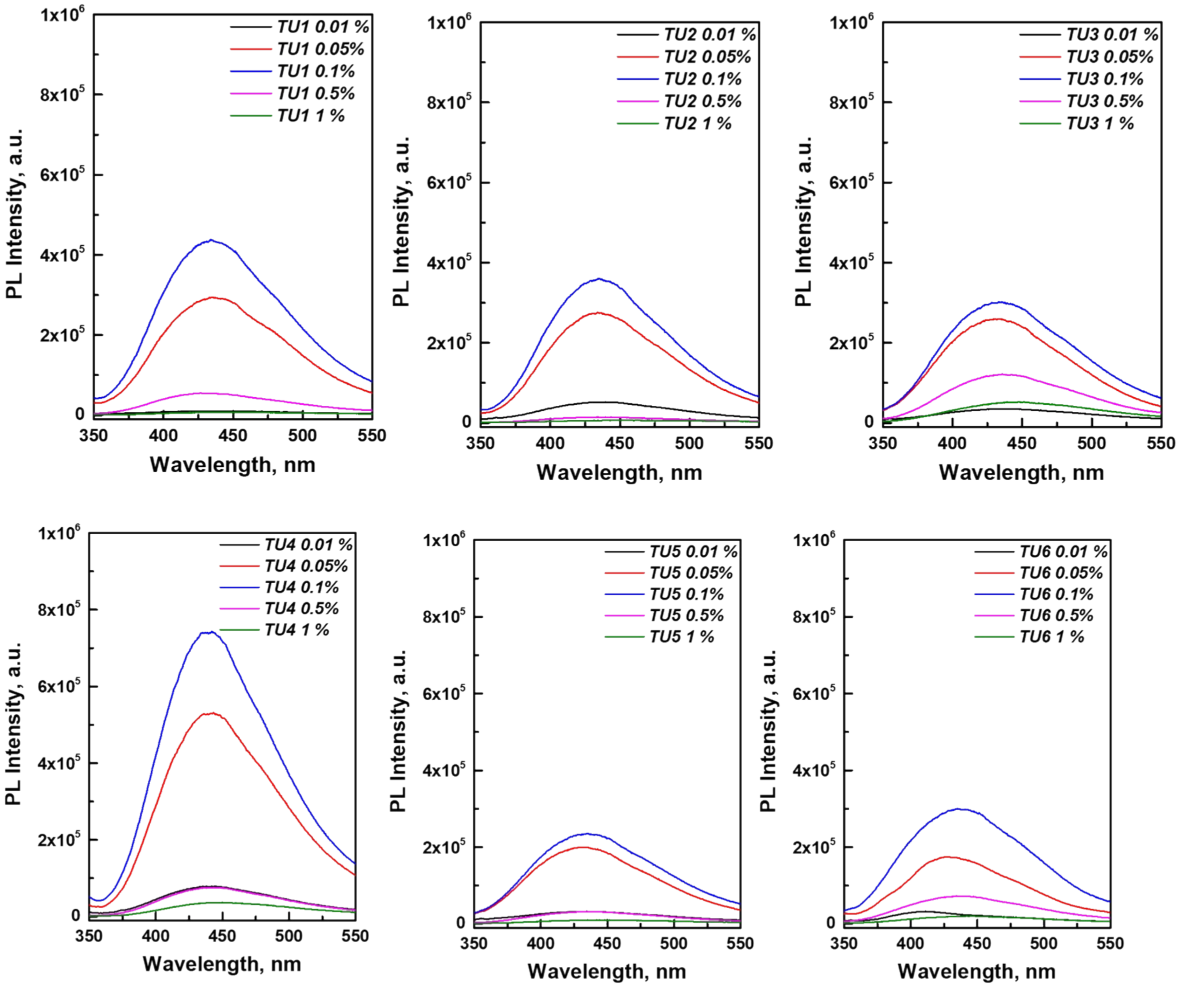


Figure S2. UV-Vis absorbance spectra of ZnS QDs synthesized by the hot-injection method from various substituted thioureas in solution.



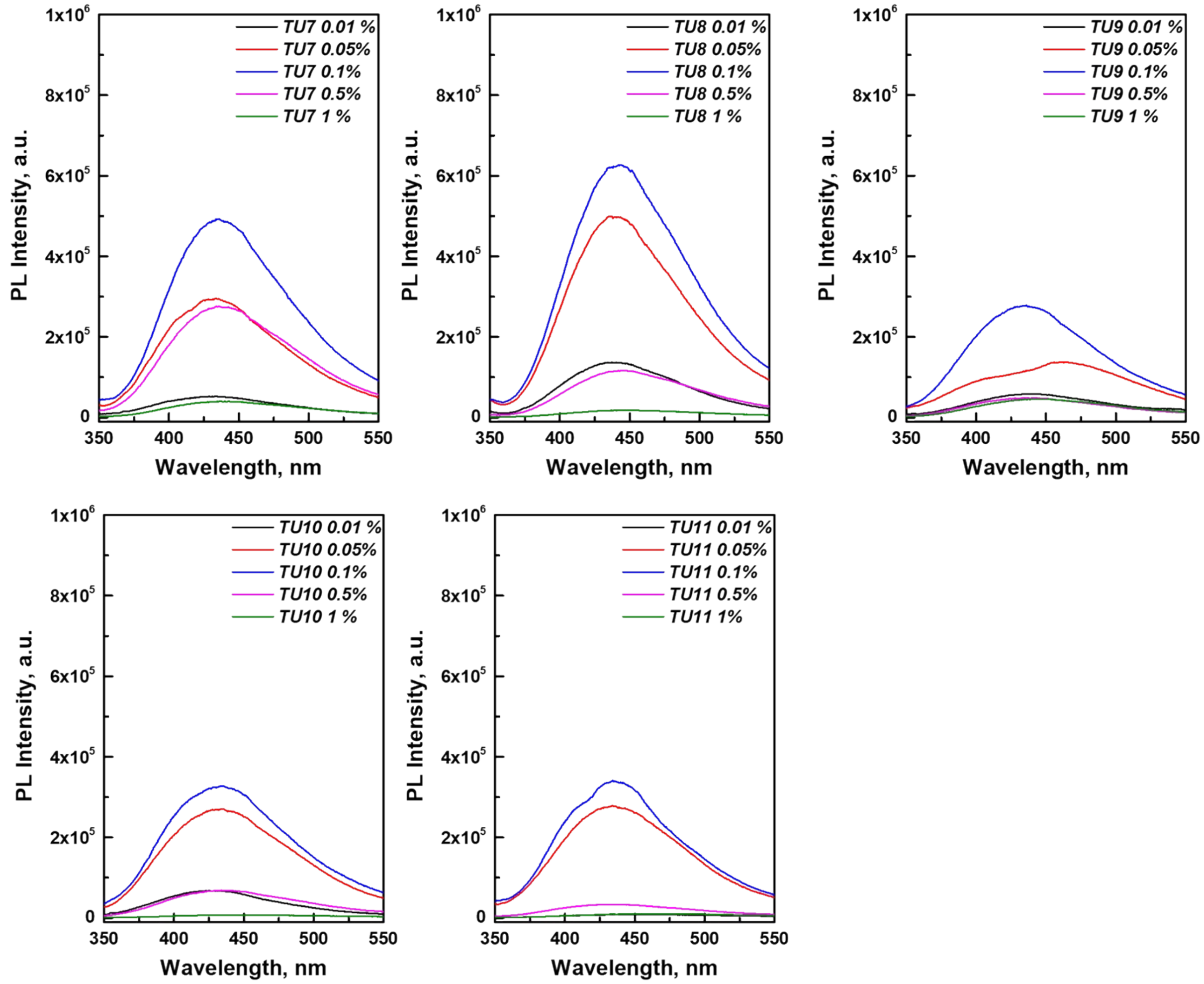


Figure S3. Photoluminescence spectra of ZnS QDs synthesized by the hot-injection method from various substituted thioureas in solution.

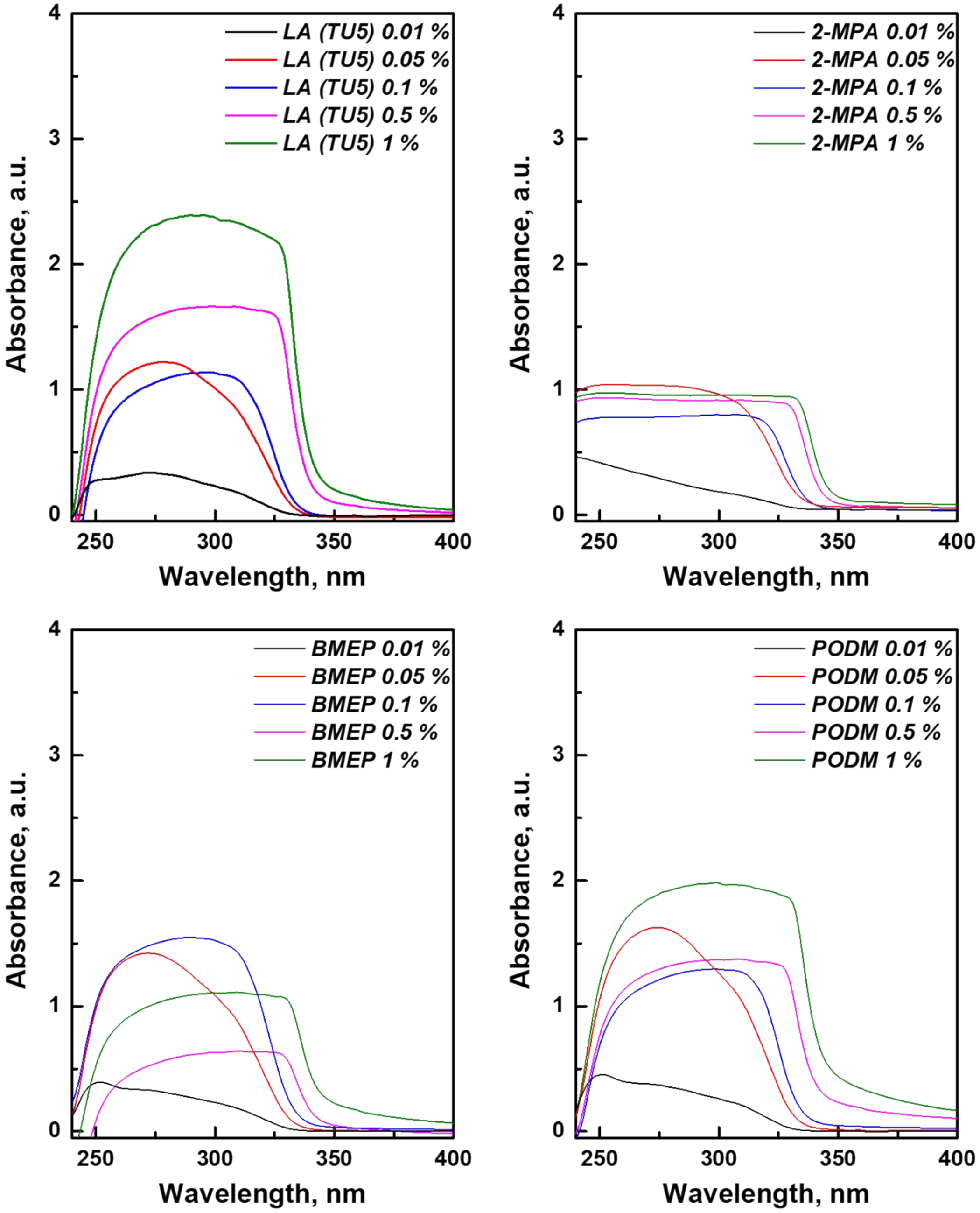


Figure S4. UV-Vis absorbance spectra of ZnS QDs synthesized by the hot-injection method from **TU5** with various capping ligands in solution.

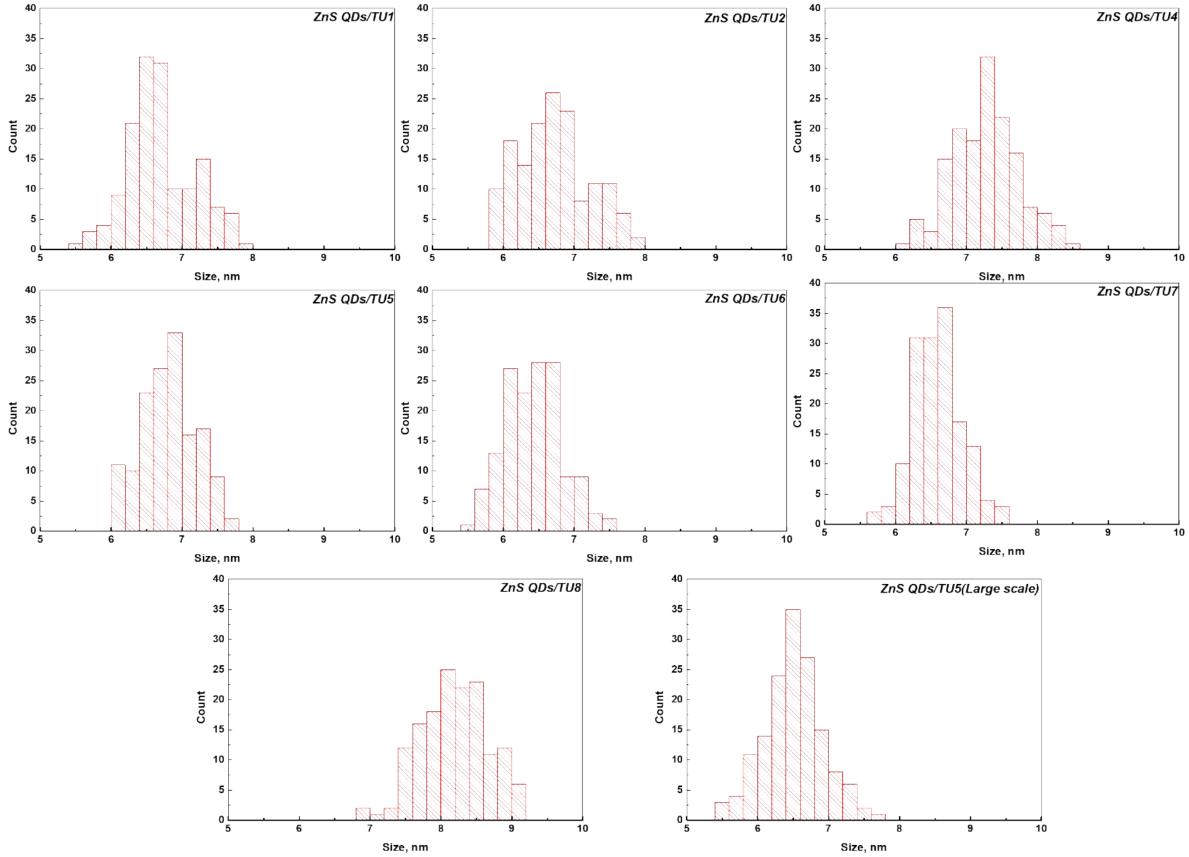
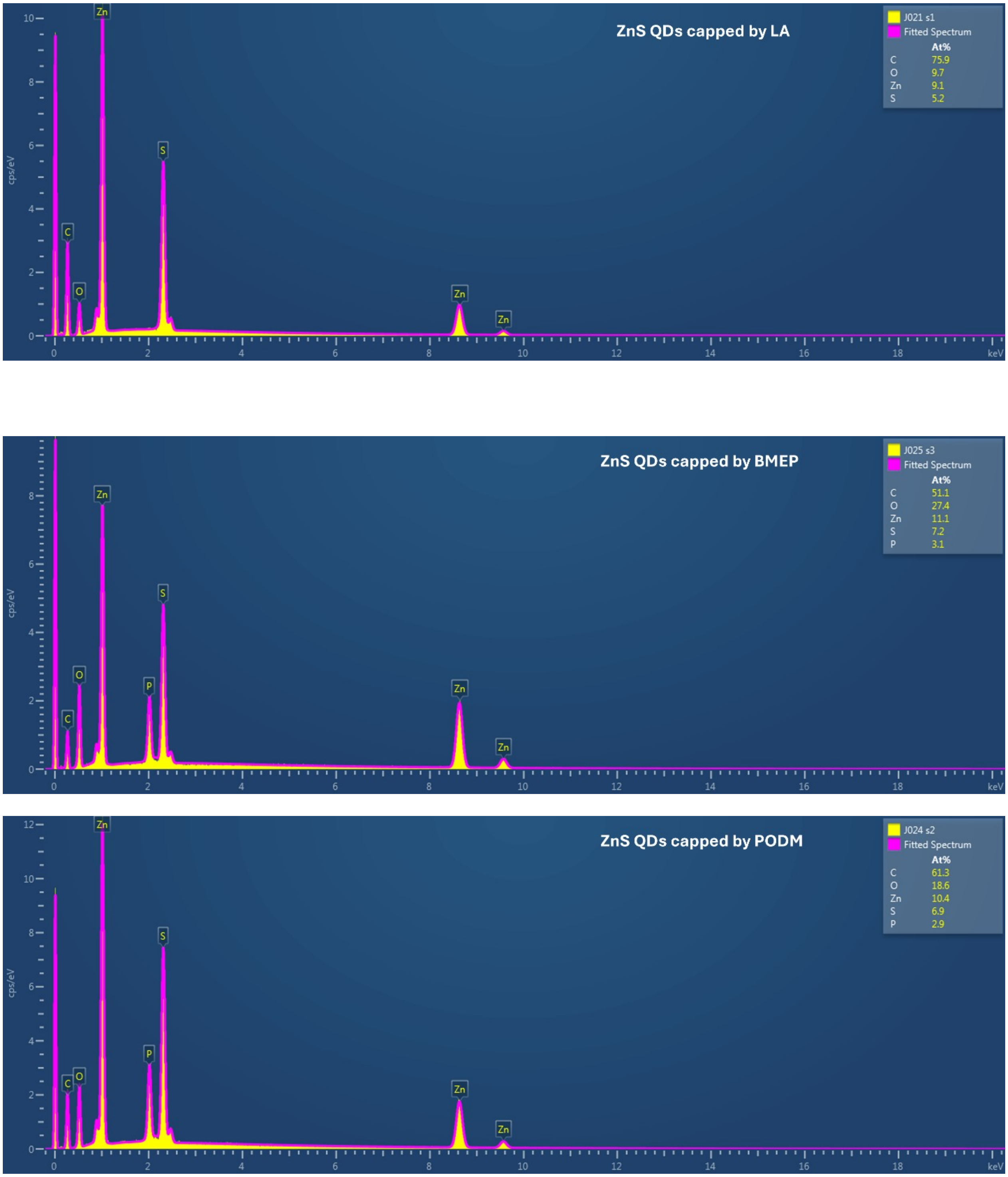


Figure S5. Size distribution histograms of ZnS QDs prepared by the hot-injection technique from substituted thioureas.

Table S2. Quantitative surface roughness parameters (R_a and R_q) derived from AFM measurements of ZnS nanocomposite thin films.

Thin films	**R_q, nm**	**R_a,nm**
ZnS/LA neat films	0.7	0.6
ZnS/2-MPA neat films	10.4	8.1
ZnS/LA dispersed in PMMA	1.5	1.2
ZnS/LA dispersed in PVK	0.5	0.4
ZnS/2-MPA dispersed in latex	2.7	2.1
ZnS/2-MPA dispersed in PEG	12	9.2
ZnS/PODM-PVK copolymer	18.7	13
ZnS/BMEP-PMMA copolymer	0.5	0.4



ZnS QDs capped by LA

ZnS QDs capped by BMEP

ZnS QDs capped by PODM

Figure S6. EDS spectra of ZnS QDs prepared by the hot-injection technique from substituted thioureas.