

# Ligand Exchange of Core/Shell CuInS<sub>2</sub>/ZnS Quantum Dots for Preparation of Their Homogeneous Ink

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## ABSTRACT

*1-Dodecanethiol on CuInS<sub>2</sub>/ZnS quantum dots (QDs) was exchanged with cyclohexanethiol. The obtained QDs were transparently dispersed in alicyclic diepoxy compound to yield the QD ink for ink-jet printing. This homogeneous dispersion is attributed to similarity in molecular structure between the ligand and the ink component.*

## 1. INTRODUCTION

QDs have a characteristic property of controlling the emission wavelength by adjusting their size, so they are applicable to color converters of displays.<sup>1</sup> In recent years, inkjet technology has attracted attention as effective patterning method of the color converting layers.<sup>2</sup> The inkjet technology is a method in which can be formed patterns by jetting curable ink droplets to substrates and curing them by heat or light. This technology has advantages over conventional photolithography technology<sup>3,4</sup> in terms of reducing QD losses and capital investment.<sup>5</sup> In order to produce the color converting layers by the inkjet technology, it is indispensable to disperse QDs uniformly in the curing component of the ink. To improve the dispersibility, it is necessary to replace the ligands on the surface of QDs with the molecules which have higher affinity against the ink component. As a method of ligand exchange, it is effective to inject a target ligand molecule directly into the QD dispersion. The surface ligands repeatedly adsorbed and desorbed on QDs in their growth process, so it is easy to exchange the ligands.<sup>6</sup> In addition, a molecule having a thiol group, which is strongly adsorbed on the QD surface, is suitable for ligand exchange.<sup>6,7</sup> In the present study, CuInS<sub>2</sub>(CIS)/ZnS QDs were used as a model material. We investigate ligand exchange of 1-dodecanthiol (DDT) for 3-mercaptopropionic acid (MPA) or cyclohexanethiol (CHT) to improve the dispersibility of QDs into the curing component, alicyclic diepoxy compound, of the ink.

## 2. EXPERIMENTAL PROCEDURE

CuI and In(CH<sub>3</sub>COO)<sub>3</sub> were added to Ar gas bubbled DDT and degassed under vacuum at 100 °C for 30 min. After introducing Ar gas into the system, the mixture was heated at 230 °C for 5 min to allow the growth of CIS core

in solution. The first and second shell solutions were individually prepared by dissolving Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O in a mixed solvent of DDT, oleic acid (OA), and 1-octadecene at 190 °C and bubbling with Ar gas. The first shell solution was added into the CIS core dispersion at a rate of ~1.0 mL min<sup>-1</sup> and heated at 250 °C for 50 min. The second shell solution was also added into the resulting dispersion and heated at 250 °C for 1 h to obtain QD-DDT. Then, MPA or CHT was added for ligand exchange and kept heating at that temperature for 15 min to obtain QD-MPA and QD-CHT, respectively. The purified QD powders prepared by repeated cycles of centrifugation and redispersion were dispersed in alicyclic diepoxy compound to yield QD inks.

## 3. RESULTS AND DISCUSSION

### 3.1 Analysis of surface ligands

Fig. 1 shows FT-IR spectra of ligand molecules and the prepared QD powders. The spectrum of QD-DDT (Fig. 1 (c)) exhibited peaks at 2930 cm<sup>-1</sup> and 2860 cm<sup>-1</sup> (No. 1, 2) assigned to the stretching vibration of C-H bond in long carbon chains of DDT and OA. These peaks were hardly observed in the spectrum of QD-MPA (Fig. 1 (e)) as a result of ligand exchange of DDT for MPA with a short carbon chain. In addition, the peak assigned to the stretching vibration of C=O bond in carboxy group of OA at 1710 cm<sup>-1</sup> (No. 3) disappeared, while the peaks of COO<sup>-</sup> asymmetric and symmetric vibrations at 1550 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> (No. 4, 5), respectively, appeared. This is attributed to coordination of the carboxy group to the metal ion of the QD surface. The similarity of the spectra of CHT (Fig. 1 (f)) and QD-CHT (Fig. 1 (g)) may reveal successful ligand exchange of DDT for CHT.

### 3.2 Photoluminescence properties

As shown in Fig. 2, the photoluminescence (PL) peaks of QD-DDT, QD-MPA, and QD-CHT were observed at 563.7 nm, 574.3 nm, and 555.0 nm under 400 nm excitation, respectively. The PL intensities of QD-MPA and QD-CHT were 9% and 65% of that of QD-DDT, respectively. These decreases may be attributed to QD deterioration by oxidation during ligand exchange.

### 3.3 Dispersibility in an alicyclic diepoxy compound

Fig. 3 shows photographs of QD dispersions in an alicyclic diepoxy compound. QD-DDT did not disperse in

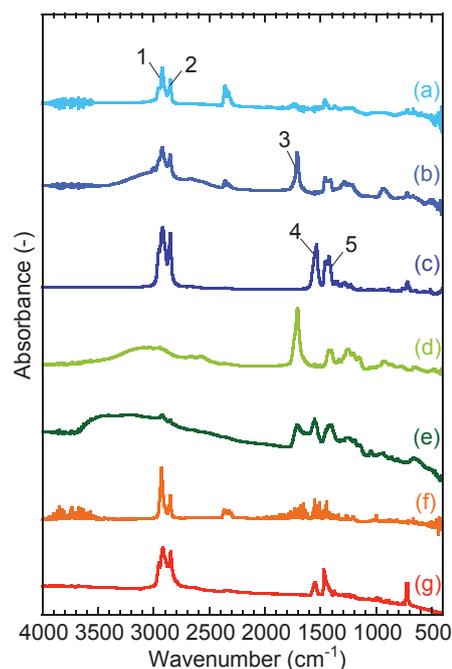
this compound (Fig. 3 (a)). A small amount of sediment was observed for QD-MPA (Fig. 3 (b)). In contrast, QD-CHT transparently dispersed without any sedimentation (Fig. 3 (c)). This homogeneous dispersion is attributed to the similarity in molecular structure between CHT and the alicyclic diepoxy compound, as confirmed from Fig. 4.

#### 4. CONCLUSIONS

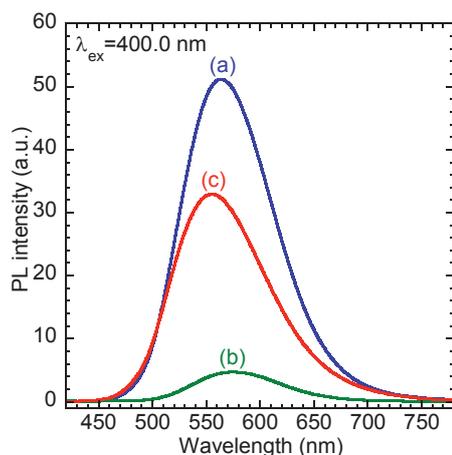
Ligands of DDT and OA on CIS/ZnS QD surface were successfully exchanged for MPA and CHT at 250 °C for 15 min to yield QD-MPA and QD-CHT, respectively. The QD-CHT was more homogeneously dispersed in an alicyclic diepoxy compound to produce the ink which could be used for ink-jet printing.

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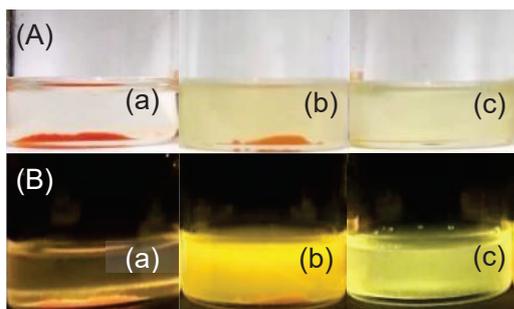
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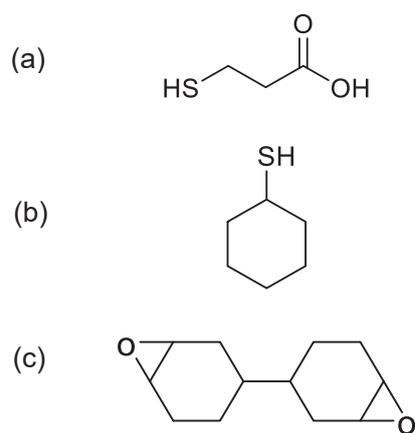
**Fig. 1** FT-IR spectra of ligand molecules and QD powders. (a) DDT, (b) OA, (c) QD-DDT, (d) MPA, (e) QD-MPA, (f) CHT, and (g) QD-CHT.



**Fig. 2** Photoluminescence spectra of QD dispersions. (a) QD-DDT in chloroform, (b) QD-MPA in tetramethylammonium hydroxide solution, and (c) QD-CHT in chloroform.



**Fig. 3** Photographs of QD inks under (A) white light and (B) 365 nm near-UV light. (a) QD-DDT. (b) QD-MPA. and (c) QD-CHT.



**Fig. 4** Molecular structures of (a) MPA, (b) CHT, and (c) the used alicyclic diepoxy compound.