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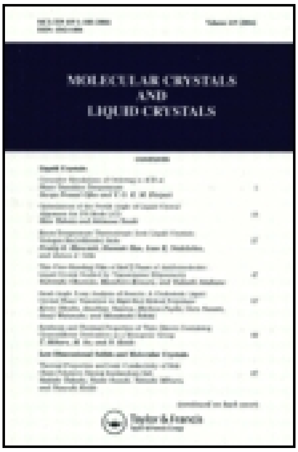

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# EuS Nano-assembles Linked with Photo-functional Naphthalenedithiols

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*Novel photo-functional naphthalenedithiol (NpDDT) as a linker molecule for formation of EuS nanocrystal assembles (EuS nano-assembles) has been reported. NpDDT is synthesized by the reaction of 1,4-dihydroxynaphthalene with 1,10-decanedithiol in benzene at 80°C for 1 hour.*

*Formation of EuS nano-assembles with NpDDT is observed by TEM measurement. Photophysical properties of EuS nano-assembles with NpDDT are characterized using the emission spectra and the emission quantum yields. The emission quantum yields of naphthalene units in NpDDT are depended on the aggregation size of EuS nano-assembles. Novel luminescent NpDDT has been reported as an effective linker material for formation and observation of semiconductor EuS nano-assembles for the first time.*

**Keywords** Aggregation; assemble; emission quantum yield; naphthalene

## Introduction

Semiconductor nanocrystals have attracted considerable attention in the area of advanced materials science because of their remarkable optical, electric, and magnetic properties [1–7]. In particular, magnetic semiconductor nanocrystals with magnetic and optical properties have potential applications including use in photo-magnetic devices as optical isolator and magneto-optical memory [8–10]. One of the most important series of intrinsic magnetic semiconductors is europium chalcogenides, EuX (X=O, S, Se, and Te) [11]. EuX is a characteristic magnetic semiconductor which is characterized by the degenerated 4f orbitals of Eu(II) ions existing between the conduction band (5d orbitals of Eu(II)) and the valence band (p orbitals of $O^{2-}$, $S^{2-}$, $Se^{2-}$, or $Te^{2-}$), and the 4f–5d electronic transition and spin configuration lead to large opto-magnetic (Faraday) effect, makes them promising candidates as an active material in future optical isolator [12]. Among of them, EuS nanocrystals have been focused as promising materials because of their ferromagnetic properties and characteristic Faraday effects in visible region [13, 14].

Recently, nano-assembles composed of semiconductor, metal or magnetic nanocrystals have been extensively studied for potential applications in fields such as photovoltaics, biological labels, and three-dimensional waveguides [15–17]. EuS nano-assembles with exciton coupling and specific magneto-interactions have also been reported [18, 19]. The optical and magnetic interactions between EuS nanocrystals are based on the formation of

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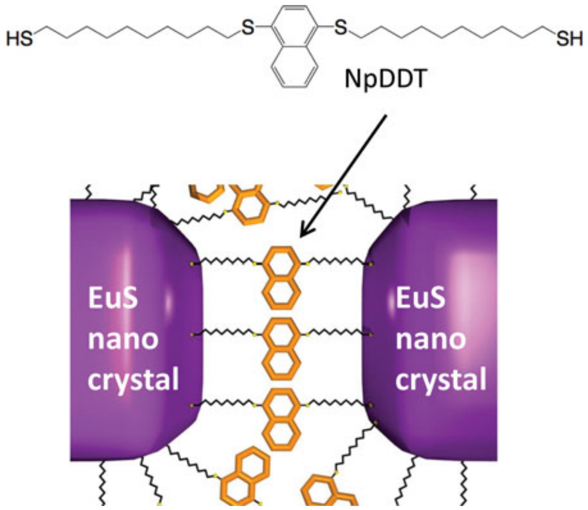

**Figure 1.** Chemical structure of naphthalenedithiol, NpDDT.

nano-assembled structures. In order to analyze the opto and magnetic interaction in EuS nano-assembles, specific functional molecule linked with EuS nanocrystals should be required. We here focus on a photo-functional naphthalenedithiol (NpDDT) as a linker for formation of EuS nano-assembles (Fig. 1). Naphthalene molecule shows photo-luminescence with highly emission quantity yield, which is dependent on surrounding environment such a dielectric constant of the matrix [20]. Dithiol unit has also been used as an ideal linker part for chemical connection between semiconductor nanocrystals and organic molecules. The NpDDT molecule is expected to be a sensing linker unit for analysis of EuS nano-assembles. NpDDT was synthesized by the reaction that hydroxyl groups of 1,4-dihydroxynaphthalene are replaced by dithiol groups [21]. Self-assembled structures of the EuS nano-assembles with NpDDT are characterized with XRD and TEM measurements. Photophysical properties of EuS nano-assembles with naphthalene are characterized using the emission spectra and the emission quantum yields. In the present study, synthesis and photophysical properties of EuS nano-assembles with photo-functional NpDDT have been demonstrated for the first time.

## Experimental

### *Materials*

Europium(III) chloride hexahydrate ($EuCl_3 \cdot 6H_2O$) and sodium *N*,*N*-diethyldithiocarbamate trihydrate ($Na(S_2CNEt_2) \cdot 3H_2O$) were purchased from Kanto Chemical Co. Inc. Tetraphenylphosphonium bromide ($BrPPh_4$) was purchased from Wako Pure Chemical Industry, Ltd. Oleylamine (OA) and 1,10-decanedithiol (DDT), 1,4-naphthalenediol and p-toluenesulfonic acid was obtained from Tokyo Chemical Industry Co., Ltd. *p*-Toluenesulfonic acid was purified by recrystallization from ethylacetate and dried under vacuum before use. All other chemicals and solvents were reagent grade and were used without further purification.

## Apparatus

FT-IR measurements were performed at room temperature by Perkin-Elmer system 2000 FT-IR spectrometer. $^1$H NMR spectra were measured by JEOL AL-300 (300 MHz). $^1$H NMR chemical shifts were determined by using tetramethylsilane (TMS) as an internal standard. XRD spectra were characterized by Bruker AXS. UV-vis absorption spectra were measured with JASCO V-570 spectrophotometer at room temperature. Emission spectra were measured with JASCO F-6300-H spectrometer and corrected for the response of the detector system. The emission quantum yields excited at 330 nm were calculated using JASCO F-6300-H spectrofluorometer attached with JASCO ILF-533 integrating sphere unit ($\phi = 100$ mm). The wavelength dependences of the detector response and the beam intensity of Xe light source for each spectrum were calibrated using a standard light source. EuS nano-assembles was identified using a transmission electron microscope (TEM) JEOL JEM-2010 FASTEM (200 kV) with an energy dispersive X-ray spectroscopy (EDS) detector. The chemical compositions of EuS nano-assembles were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Shimadzu ICPE-9000) and the EDS analysis.

## Synthesis

*Synthesis of Tetraphenylphosphonum Tetrakis(diethyldithiocarbamate) Europium(III) ((PPh$_4$)[Eu(S$_2$CEt$_2$)$_4$]).* A solution of ($Na(S_2CNEt_2)\cdot 3H_2O$) (14 g) in 30 mL of methanol was added to $EuCl_3\cdot 6H_2O$ (5.6 g) dissolved in 30 mL of methanol while stirring and reacted for 3 h. After the reaction mixture was filtered, a solution of $BrPPh_4$ (6.4 g) in 30 mL of methanol was added to the filtrated solution and stirred for 9 h. The resulting precipitate was separated by filtration and washed 2 times with ethanol. Yield: 30%. FT-IR spectrum (KBr): 1485 – 1482 (C–N) cm$^{-1}$, 1442 (P–Phenyl) cm$^{-1}$, 1007 (C–S) cm$^{-1}$. $^1$H NMR spectrum (ppm, $CDCl_3$): 1.61 (q, $J = 7$ Hz, 12H), 3.17 (q, $J = 7$ Hz, 8H), 7.70 (m, 16H), 7.91 (t, $J = 6.3$ Hz, 4H). Anal. Calcd for $C_{44}H_{60}EuN_4PS_8$: C, 48.73; H, 5.58; N, 5.17; S, 23.65%. Found: C, 48.55, H, 5.51, N, 5.00, S, 23.41%.

*Preparation of Cube-Shaped EuS Nanocrystals, EuS-OA.* Under $N_2$ atmosphere, ($PPh_4$)[$Eu(S_2CNEt_2)_4$] (0.5 g) was dissolved into oleylamine (4.5 g), and the mixture was heated at 180°C and stirred for 20 min. After the reaction solvent was heated to 300°C and stirred for 6 h, the purple liquid was centrifuged at 4000 rpm for 10 min. The precipitation was added to 8 mL of chloroform and centrifuged at 4000 rpm for 15 min, and the clear purple liquid of oleylamine capped EuS nanocrystals (EuS-OA) was obtained.

*Synthesis of 1,4-bisdecanethionaphtalene, (NpDDT).* 1,4-bisdecanethionaphtalene. NpDDT, was prepared by the similar method as previously reported [21]. Under $N_2$ atmosphere, 1,4-dihydroxynaphthalene (0.81 g, 5 mmol), *p*-toluenesulfonic acid (0.48 g, 2.5 mmol) and 1,10-decanedithiol (10 mL, 46 mmol) were dissolved into benzene (50 mL), and the mixture was refluxed at 80°C for 1 h. After aqueous workup, the product was purified by column chromatography on silica gel using ethylacetate as an eluent. The collected product was crystallized from a mixture of ethylacetate and hexane to give NpDDT as a white solid. FT-IR spectrum (KBr): 2924, 2849 (C–H) cm$^{-1}$, 2567 (S–H) cm$^{-1}$, 1564 (C=C of Ar) cm$^{-1}$, 1466 (C–H) cm$^{-1}$. $^1$H NMR spectrum (ppm, $CDCl_3$): 1.2–1.4 (m, 26H), 1.5–1.7 (m, 8H), 2.5–2.6 (m, 4H), 2.9–3.0 (m, 4H), 7.5 (s, 2H), 7.5–7.6

(m, 2H), 8.4–8.5 (m, 2H). Anal. Calcd for $C_{30}H_{48}S_4$: C, 67.10; H, 9.01; N, 0; S, 23.89%. Found: C, 66.87, H, 9.06, N, 0.00, S, 24.00%.

*Preparation of EuS Nano-assembles, EuS-NpDDT-20 min and EuS-NpDDT-3 h.* EuS nano-assembles were formed by adding NpDDT (0.14 g, 0.25 mmol) dissolved in 10 mL of THF to a solution of 0.03 g of EuS-OA dissolved in 120 mL of THF. After the reaction solvent was stirred at room temperature for 20 min (EuS-NpDDT 20min) and 3 h (EuS-NpDDT-3 h), the resulting solution was centrifuged at 4000 rpm for 10 min. The precipitation was added to 20 mL of chloroform and EuS nano-assembles were obtained.

*Preparation of Polymer Thin Films Containing EuS Nano-assembles.* The obtained EuS nano-assembles (20 mg) were added to a chloroform solution (1 mL) of polymethylmethacrylate (PMMA) (2.0 g) and dispersed well under ultrasonic treatment, giving the colloidal suspension. The PMMA thin films were prepared on a glass substrate from the colloidal suspension using drop-casted method for measurements of photophysical properties. The thickness of the PMMA thin films containing EuS nano-assembles were measured by a surface profiler KLA Tencor ALPHA STEP 500.

## Results and Discussion

### *Formation of EuS Nano-assembles*

The cube-shaped EuS nanocrystal with oleylamine, EuS-OA, were prepared by the thermal reduction of the single source precursor, $(PPh_4)[Eu(S_2CNEt_2)_4]$, in oleyleamine under $N_2$ atmosphere at 300°C for 6 hours. XRD confirmed the formation of crystalline EuS NCs. Diffraction peaks $2\theta$ of XRD measurement = 25.5, 29.8, 42.6, 50.6, 53.1, 62.1, and 70.5° were assigned(111), (200), (220), (222), (400), (420), and (422) of NaCl type EuS, respectively. The crystal grains of EuS-OA calculated using the Scherer equation from XRD spectra were found to be 18 nm. Typical TEM images of EuS-OA are shown in Fig. 2a. Cubic-shaped images were observed and their electron diffraction pattern was found to be a good agreement with the isometric EuS lattice. The crystal size evaluated by the TEM observations was found to be approximately 18 nm and similar to the size measured by XRD (18 nm). Naphthalenedithiol, NpDDT, is a promissing photo-functional linker with luminescent naphthalene unit and dithiol parts as a linker for formation of EuS

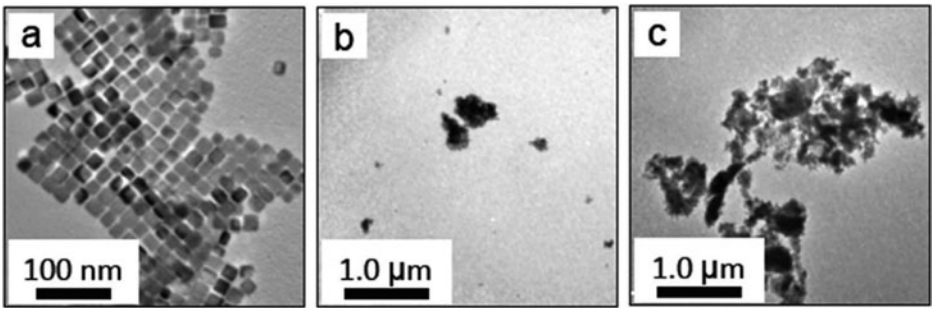

**Figure 2.** TEM images of a) EuS-OA nanocrystals, b) EuS-NpDDT-20 min, and c) EuS-NpDDT-3 h.

nano-assembles. NpDDT was synthesized by the reaction of 1,4-dihydroxynaphthalene with 1,10-decanedithiol in benzene at 80°C for 1 hour.

Prepared NpDDT linkers were added into THF solution of EuS-OA at room temperature for 20 min (EuS-NpDDT-20 min) and 3 hours (EuS-NpDDT-3 h). Each THF solution containing EuS-NpDDT-20 min or EuS-NpDDT-3 h was separated by centrifugation and re-dispersed into chloroform. The TEM images of EuS-NpDDT-20 min and EuS-NpDDT-3 h are also shown in Figs. 2b and c, respectively. The aggregation size of EuS-NpDDT-3 h was estimated to be greater than 1000 nm. We observed that average aggregation size of EuS-NpDDT-3 h was much larger than that of EuS-NpDDT-20 min. We consider that aggregation growth of EuS nano-assembles is dependent of the replacement reaction time of NpDDT from oleylamine on the EuS nanocrystals surface. In order to confirm the chemical bonding of EuS-S-Np-S-EuS, we carried out measurements of absorption bands of EuS using the UV-vis absorption spectra (Fig. 3a). The characteristic red-shifts in UV-vis spectra of EuS-S-Np-S-EuS nano-assembles were observed, and were depended on the replacement time of oleylamine with NpDDT. We consider that the red-shifts are directly linked to binding energy, in other words, ligand field of Eu(II) ions on the EuS surface. Binding energy of Eu-NpDDT might be larger than that of Eu-oleylamine. Thus, energy gap of *4f-5d* bands in Eu-NpDDT may be smaller than that in Eu-oleylamine. We have measured concentration

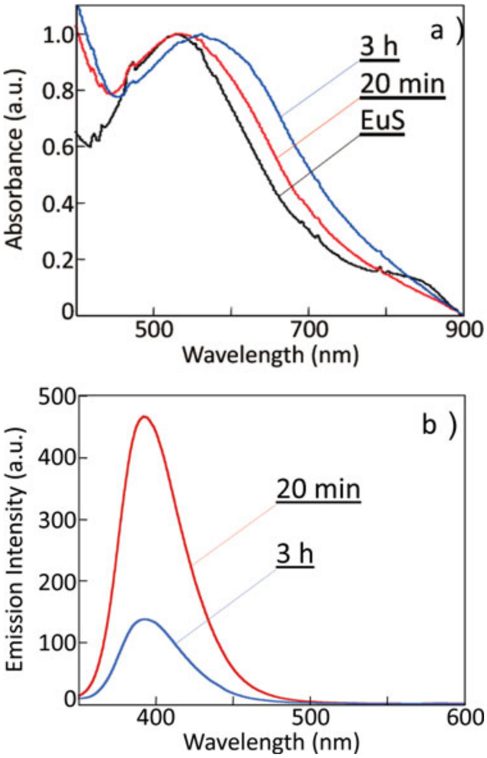

**Figure 3.** a) UV-vis absorption spectra of PMMA thin films containing EuS nanocrystals, EuS-NpDDT-20 min and EuS-NpDDT-3 h. b) Emission spectra of PMMA thin films containing EuS-NpDDT-20 min and EuS-NpDDT-3 h. The emission spectra were measured by excitation at 330 nm at room temperature.

ratio of Eu and S using inductively coupled plasma optical emission spectroscopy (ICP-OES). EuS-NpDDT-3 h shows that Eu/S ratio is found to be 1/2.2, although Eu/S value in EuS nanocrystals using EDS analysis is 1/1. Since NpDDT has two sulfur atoms in one molecule, EuS/NpDDT is estimated to be 1/0.6. Here, we calculated the number of atom in cube-shaped EuS nanocrystals (average diameter: 18 nm). Total amount of Eu atoms in EuS nanocrystals is approximately 100,000 atoms, in contrast, the number of Eu atoms on the EuS surface ($\mathrm{Eu}_{\mathrm{surface}}$) is 10,000 atoms. From these estimations, we found excess amount of NpDDT on the EuS surface ($\mathrm{Eu}_{\mathrm{surfac}}/\mathrm{NpDDT} = 1/6$), although we had carried out the purification of EuS-NpDDT using centrifugation of THF solution. Oleylamine molecules on EuS nanocrystals might be replaced by large amount of NpDDT molecules. On the other hand, peak-top wavelength of *4f-5d* transition band in EuS-NpDDT-20 min is much similar to that in EuS-oleylamine. We consider that surface of EuS-NpDDT-20 min might be covered with large amount of oleylamine.

### Photophysical Properties of EuS Nano-Assembles

In order to analyze photophysical properties of the EuS nano-assembles, we prepared PMMA thin films including EuS-NpDDT-20 min or EuS-NpDDT-3 h. The emission spectra of PMMA thin films excited at 330 nm are shown in Fig. 3b. The emission spectra are normalized at the absorption bands of the $\pi-\pi^*$ transition of naphthalene units in NpDDT linkers. We observed the characteristic emission band at 392 nm, which is also assigned to the $\pi-\pi^*$ transition of naphthalene units. The emission intensity of PMMA thin film with EuS-NpDDT-3 h is much smaller than that with corresponding EuS-NpDDT-20 min. We also found that the emission wavelength of NpDDT molecule excited at 330 nm in chloroform is found to be 403 nm, which is longer than those of NpDDT linkers in PMMA thin films with EuS nano-assembles. The characteristic red-shift of the emission spectrum of naphthalene unit in PMMA films with EuS nano-assembles might be affected by aggregation of NpDDT units on the EuS nanocrystal surface.

The emission quantum yields of NpDDT and PMMA thin films with EuS-NpDDT-20 min and EuS-NpDDT-3 h are summarized in Table 1. The emission quantum yield of NpDDT excited at 330 nm in chloroform was found to be 16%. On the other hand, the emission quantum yields of PMMA thin films with EuS-NpDDT-20 min and EuS-NpDDT-3 h were estimated to be 11 and 6%, respectively. The excited state of naphthalene units in NpDDT may be quenched by adsorption of EuS nanocrystals, because of their broad

**Table 1.** Emission properties of NpDDT in chloroform and PMMA thin films with EuS-NpDDT-20 min and EuS-NpDDT-3 h

| Sample | Matrix | Emission Wavelength/nm | Emission quantum Yield /% |
|---|---|---|---|
| NpDDT | chloroform | 403 | 16 |
| EuS-NpDDT-20 min | PMMA | 392 | 11 |
| EuS-NpDDT-3 h | PMMA | 392 | 6 |

*Note*. The emission quantum yields were measured by excitation at 330 nm at room temperature. PMMA film thickness using surface profiler was found to be 10 $\mu$m.

absorption bands at around 400 nm. We also note that the emission quantum yield of EuS-NpDDT-3 h with larger aggregation size is smaller than that of EuS-NpDDT-20 min. The emission quantum yield of NpDDT might be related to size of EuS nano-assembles.

## Conclusions

We have successfully observed the aggregation growth of EuS nanocrystals using luminescent NpDDT linkers. Novel luminescent NpDDT linker is an effective material for formation and observation of EuS nano-assembles. The emission quantum yields of naphthalene units in NpDDT are depended on the aggregation size of EuS nano-assembles. Quenching mechanism of the emission process of naphthalene molecules on semiconductor nano-assembles have not been reported at the present time. We are now trying to analyze the emission process of NpDDT attached with EuS nanocrystals using EuS nano-assembles in various organic solvents.

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