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Thermo-stable lanthanide coordination nanoparticles composed of luminescent Eu(III) complexes and organic joint ligands using micelle techniques in water

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Abstract: Strong luminescent nanoparticles composed of lanthanide coordination polymers using micelle reaction techniques, lanthanide coordination nanoparticles,arereported.Size of the nanoparticles estimated using dynamic light scattering measurements were found to be approximately 66nm. Lanthanide coordination nanoparticles were characterizedusing ESI-MS spectrometry, XRD measurements and thermogravimetric analyses (TGA). Emission properties of lanthanide coordination nanoparticles were estimated using emission spectra and emission lifetimes. These results indicate that nanoparticles composed of lanthanide coordination polymers show effective luminescent properties and thermal stability such as bulk powders of lanthanide coordination polymers.

Introduction:

Lanthanide complexeswith narrow emission bands and long emission lifetimes have beenregarded as promising luminescent materials for use in electroluminescent optical materials,[1] organic light-emitting diodes(OLEDs),[2] and luminescent bio-sensing applications.[3] At the present stage, various types of luminescent lanthanide complexes have been reported.[4] Plastic luminescent materials containing lanthanide complexes have been also studied in the field of industrial application, such as luminescent sealing films for solar cells[5] and plastic optical waveguides for opto-telecommunication

systems.[6] Thermal stability of the luminescent plastic materials are required that industrial preparation under high temperature at around 250 ^{o}C should be useful in molding process of their materialsand solder dissolution process for construction of electronic devices.Industrial molding and soldering processes under high temperature should be used for modern manufacturing process.

Based on the view points, luminescent lanthanide coordination polymers have been recently focused as the thermal stable luminescent materials.The lanthanide coordination polymers are composed oflanthanide complexes bridged organic coordination parts periodically,these periodical structures are combined withchemical binding such as CH-π and CH-F interactions.The periodical structures lead to improvement of thermal stability with suppression of thermal relaxation under high temperature. Previously, Reddy has reported thermally stable Lanthanide coordination polymers with 4-(dipyridine-2-yl)aminobenzoate ligands(decomposition point = 450 ^{o}C).[7] Guo has also described metal-organic frame works composed of Tb(III) ion with 1,4-Benzendicarboxylic acid(decomposition temperature = 400 ^{o}C).[8] However, those lanthanide coordination compoundsshow low emission quantum yield less than 20 %.The emission quantum yield is improved by control of vibrational frequency and geometrical structures in lanthanide coordination polymers. We haverecently reported

thermo-stable lanthanide coordination polymers with high emission quantum yield.[9] The lanthanide coordination polymersare composed ofhfa(hexafluoroacetylacetonate) ligands for suppression of vibrational relaxation[10] and phosphine oxide ligands for formation of asymmetric coordination structures.[11] The emission quantum yield and decomposition pointof Eu(III) coordination polymer attached with dpbp (4,4'-bis(diphenylphosphoryl)biphenyl) are found to be 83 % and 308 ^{o}C, respectively.[9]

In general, characteristic tight-stacking structures of lanthanide coordination polymers lead to formation of insoluble compounds, micro-sized particles, in water and organic solvents. Their insoluble micro-sized particles prevent preparation of transparent materials for optical usebecause of their multiple light scattering in UV-Vis region. The nano-sized particles of lanthanide coordination polymers without multiple light scattering may provide future optical and luminescent materials. According to the preparation of organomolecule nanoparticles, buildup and breakdown methods have been reported. Nakanishi and Oikawa have described reprecipitation method for formation of perylene nanocrystals.[12] Masuhara and Asahi have presented laser ablation method in liquid media for preparation of organic dyes and pigments nanoparticles.[13] Preparations of lanthanide coordination nanoparticles assisted with surface stabilizers have been reported.[14, 15] Kimizuka has also successfully reported lanthanide

coordination nanoparticles using supramolecular networks.[16]

We here focused on characteristic formation of organo-nanoparticles using micelle technique in liquid media, such as preparation of nano scaled organic compounds. The preparations of polystyrene nanoparticles using micelle techniques have been reported in the field of polymer science.[17] The micelle sizes are also controlled by concentration and molecular structure of organo-surfactants in water media.[18]

In the present study, strong luminescent nanoparticlescomposed of lanthanide coordination polymers, lanthanide coordination nanoparticles, are reported. The luminescent nanoparticles are obtained by the polymerization of $Eu(hfa)_3(H_2O)_2$ (hfa:hexafluoroacetylacetonate) with joint ligands (dpbp:4,4'-bis(diphenylphosphoryl)biphenyl) in micelles under water. The particle size is controlled using SDS (sodium lauryl sulfate) and TMOA (n-Octyltrimethylammonium Bromide) in water solution(Figure1). The structure of nanoparticles was characterized using ESI-MS spectrometry, XRD measurements. The sizes of prepared micelles were measured usingdynamic light scattering (DLS) measurements. Emissionproperties of nano-sized lanthanide coordination polymers were estimated using emission spectraand emission lifetimes. In this study, Lanthanide coordination nanoparticles are demonstrated.

Experimental

Materials. Europium acetate monohydrate (99.9%), sodium lauryl sulfate (SDS:99%) were purchased from Wako Pure Chemical IndustriesLtd. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione, 4,4’-dibromobiphenyl (>98%), n-Octyltrimethylammonium Bromide (TMOA:>98%) were obtained from Tokyo Kasei Organic Chemicals. All other chemicals and solvents were reagent grade and were used without further purification.

Apparatus. Infrared spectra were recorded with a JASCO FTIR-350 spectrometer. ^{1}H NMR (270 MHz) spectra were recorded with a JEOL EX-270 spectrometer. Chemical shifts are reported in ppmand are referenced to an internal tetramethylsilane standard for 1H NMR spectroscopy. Elemental analyses were performed with a Yanaco CNH MT-6 analyzer. Mass spectrometry were performed with a JEOL JMS-T100LP. Size-distribution were measured with a BECKMAN COULTER DelsaNanoHC. Thermogravimetric analysis (TGA) was performed on Rigaku TermoEvo TG8120 analyzer. Scanning electron microscopy (SEM) was performed by JEOL JSM-6510LA (acceleration voltage, 10 kV).

Tris(hexafluoroacetylacetonato)europium Dihydrate [$Eu(hfa)_3(H_2O)_2$]:

Europium acetate monohydrate (5.0 g, 13 mmol) was dissolved in distilled water (20

mL) in a 100 mL flask. A solution of1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7.0 g, 34 mmol) was added dropwise to the solution.The reaction mixture produced a white-yellow precipitate after stirring for 3h at room temperature. The powder was collected by filtration and recrystallized from methanol/water to afford colorless needle crystals of the title compound, yield 9.6 g (95%). IR (KBr): 1650 (s, C=O), 1145–1258 (s, C–F) cm^{-1}. $C_{15}H_7EuF_{18}O_8$ (809.91): calcd. C 22.48, H 0.88; found C 22.12, H 1.01.

4,4'-bis(diphenylphosphoryl)biphenyl (dpbp): 4,4'-bis(diphenylphosphoryl)-biphenyl was synthesized according to the published procedure.[9] A solution of n-BuLi (9.3 mL, 1.6 M hexane, 15mmol), was added dropwise to a solution of 4,4'-dibromobiphenyl (1.9 g, 6.0 mmol) in dry THF (30 mL) at -80^{o}C. The addition was completed in ca. 15 min during which time a yellow precipitate was formed. The mixture was allowed to stir for 3h at -1^{o}C, after which a PPh_2Cl (2.7 mL, 15 mmol) was added dropwise at -80 ^{o}C. The mixture was gradually brought to room temperature, and stirred for 14h. The product was extracted with ethyl acetate, the extracts washed with brine for three times and dried over anhydrous $MgSO_4$. The solvent was evaporated, and resulting residue was washed with acetone and ethanol for several times. The obtained white solid and dichloromethane (ca. 40 mL) were placed in a

flask. The solution was cooled to 0 ^{o}C and then 30 % H_2O_2 aqueous solution (5 mL) was added to it. The reaction mixture was stirred for 2h. The product was extracted with dichloromethane, the extracts washed with brine for three times and dried over anhydrous $MgSO_4$. The solvent was evaporated to afford a white powder. Recrystallization from dichloromethane gave white crystals of the titled compound.

Yield: 1.1 g (33%). IR(KBr): 1120 (st, P=O) cm^{-1}.^{1}H NMR (270 MHz, $CDCl_3$, 25^{o}C) δ7.67-7.80 (m, 16H; P-C_6H_5, C_6H_4), 7.45-7.60 (m, 12H; P-C_6H_5, C_6H_4) ppm. ESI-Mass (m/z) = 555.2$[M+H]^+$. Anal. Calcd for $C_{36}H_{28}O_2P_2$: C, 77.97; H, 5.09%. Found: C,77.49; H, 5.20%.

Preparations of micelle A, micelle B, mixed micelle C, and nanoparticles composed of lanthanide coordination polymers: TMOA (0.5g, 1.98mol) was dissolved in distilled water (10 mL) in a 100 mL flask. Diethyl ether solution (0.2 mL) of $Eu(hfa)_3(H_2O)_2$ (10mg, 12.3 μmol) was added at room temperature, resulting in formation of micelle A composed of TMOA and $Eu(hfa)_3(H_2O)_2$ in water.In contrast, SDS (0.3g, 1.04mol) was dissolved in distilled water (10 mL) in a 100 mL flask. Dichloromethane solution (0.2 mL) of dpbp (10mg, 18.0 μmol) was added at room temperature, resulting in formation of micelle B composed of SDS and dpbp in water.

Mixed micelle C was prepared by the micelle-fusion of micelle A (10mL) with

micelle B (10mL) for 4h at room temperature. Obtained micelle **A**, **B**, and **C** characterized using DLS measurements.Obtained micelle **C** were centrifuged at 4000 rpm for 20 minutes and the white powder of nanoparticles composed of $[Eu(hfa)_3(dpbp)_2]_n$ were prepared. Nanoparticles were washed twice with dichloromethane, and then characterized using XRD, DLS, ESI-MS measurements.

ESI-MS in MeOH: m/z calcd. $[Eu(hfa)_2(dpbp)]$ 1122.2, $[Eu(hfa)_2(dpbp)_2]$ 1677.4, $[Eu(hfa)_5(dpbp)_2]$ 2452.5; found $[Eu(hfa)_2(dpbp)]$ 1121.1, $[Eu(hfa)_2(dpbp)_2]$ 1676.2, $[Eu(hfa)_5(dpbp)_2]$ 2447.2. XRD and DLS data are explained in the "Result & Discussion"

Optical Measurements. The emission spectra of the lanthanide coordination polymers were measured with a JASCO F-6300-H spectrometer and corrected for the response of the detector system. The emission lifetimes of the lanthanide coordination polymers (10 mm in acetone-d_6) were measured by using the third harmonic (355 nm) of a Q-switched Nd:YAG laser [Spectra Physics, INDI-50, full width at half maximum (fwhm) = 5 ns, λ = 1064 nm] and a photomultiplier (Hamamatsu photonics, R5108, response time 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope(Sony Tektronix, TDS3052, 500 MHz) synchronized to the singlepulse excitation. The emission lifetimes were determined from theslope of logarithmic plots

of the decay profiles.

Results & Discussion

Size of micelles and lanthanide coordination nanoparticles. Lanthanide coordination nanoparticles are prepared using micelle techniques in water. The synthetic scheme is shown in Figure 1. Prepared micelle **A** (TMOA and $Eu(hfa)_3(H_2O)_2$), micelle **B** (SDS and dpbp) and mixed micelle **C** were characterized using dynamic light scattering (DLS) measurements. These size distributions are shown in Figure2a, b and c (scattering intensities of DLS: see supporting information Figure S1). The maximum distributions of micelle **A** and **B** were calculated to be 14 nm and 10 nm, respectively. Distributions of nano-aggregates composed of micelle **A** were also observedat around 109 nm (average size). Size-distribution of micelle **A** is broad, although that of micelle **B** is narrow. These size-distribution may be depended on the hydrophilicity of the materials ($Eu(hfa)_3(H_2O)_2$ and dpbp) and surfactants (TMOA and SDS). We found that the maximum distribution ofmixed-micelle **C** was estimated to be 134 nm with wide distribution. The larger size of mixed-micelle **C** might be caused by reconstruction of micelle shells composed of SDS and TMOA. The reconstruction of micelle shells lead to formation of $[Eu(hfa)_3(dpbp)_2]_n$ in micelle **C**. In order to analyze formation of nanoparticles of $[Eu(hfa)_3(dpbp)_2]_n$, we separated from nanoparticles from excess

amount of surfactants SDS and TMOA using centrifugation with dichloromethane. The particles without excess amount of surfactants are shown in Figure 2d. Average particle sizes were estimated to be 66 nm and 271 nm, respectively. Lager size distribution might be caused by aggregation of smaller nanoparticles. The SEM image is shown Figure 2e. We successfully observed formation of nanoparticles (average size: 66 nm) using micelle reaction techniques in water media.

Structure and Thermal stability of lanthanide coordinationnanoparticles. The powder XRD patterns of nanoparticles containing Eu(III) complexes is shown in Figure3a. All signals are calibrated by the signal of silicon powder at 28.4 ^{o}. Observed signals at 7.5 ^{o}, 8.8 ^{o}, 9.4 ^{o}, 10.2^{o}, 20.1 ^{o} and 21.4 ^{o} are attributed to the geometrical structures of $[Eu(hfa)_3(dpbp)]_n$. We found that the signals of nanoparticles agree with those of previously reported $[Eu(hfa)_3(dpbp)]_{n.}$[19] These results indicate that the geometrical structure of nanoparticles are the same as those of $[Eu(hfa)_3(dpbp)]_n$ (see supporting information Figure S~~1~~2). Form these results, prepared nanoparticles containing Eu(III) complexes are identified as a $[Eu(hfa)_3(dpbp)]_n$.

The thermal stability of nanoparticles composed of lanthanide coordination polymers were evaluated using thermogravimetric analyses (Figure3b). The decomposition temperature of lanthanide coordination nanoparticles was estimated to be

301^{o}C, and agreed well with that of bulk powders. We found that nanoparticles composed of $[Eu(hfa)_3(dpbp)]_n$ show effective thermal stability based on the characteristic rigid structure of $[Eu(hfa)_3(dpbp)]_n$ with CH/π and CH/F interactions.[9] The lanthanide coordination nanoparticles might be useful for industrial molding and soldering processes under high temperature for modern manufacturing process.

Emission properties of lanthanide coordinationnanoparticles. The emission spectra of lanthanide coordination nanoparticles is shown in Figure a. Emission bands for the Eu(III) coordination polymers are observed at 578, 592,613, 650, and 698 nm and are attributed to the 4f–4f transitions of $^5D_0$–^7F_J with J = 0, 1, 2, 3, and 4, respectively. The spectra are normalized with respect to the magnetic dipole transition intensities at 592 nm (Eu(III):$^5D_0$–$^7F_1$), which is known to be insensitive to the surrounding environment of the lanthanide ions. The emission spectra of nanoparticles of lanthanide coordination polymers are similar to those of bulk powders of lanthanide coordination polymers. This result indicates that the coordination geometry of lanthanide coordination nanoparticles agrees well with that of bulklanthanide coordination polymers.

The time-resolved emission profiles of the lanthanide coordination polymers also revealed single-exponential decays with lifetimes in the millisecond timescale as shown

in Figure 4b (nanoparticles). The emission lifetimes were determined from the slopes of the logarithmic plots of the decay profiles. Emission life times of nanoparticles (Figure 4b) were found to be 0.91±0.01 ms, which is the same as that of bulk powders (Figure S4b: 0.91±0.01 ms). We consider that the emission properties of nanoparticles composed of lanthanide coordination polymers are the same as those of bulk lanthanide coordination polymers.

Conclusion

We successfully prepared lanthanide coordination nanoparticles composed of luminescent Eu(III) complexes and organic joint ligands using micelle reaction techniques in water media. The thermo-stable nanostructures were characterized using DLS, XRD and TGA measurements. Emission properties of lanthanide coordination nanoparticles are similar to those of bulk powders of lanthanide coordination polymers. These results indicate that lanthanide coordination nanoparticles show effective luminescent properties and thermal stability such as bulk powders of lanthanide coordination polymers. Lanthanide coordination nanoparticles also improve the optical transmittance because of their decrease of multiple light scattering in UV-Vis region. Strong luminescent nanoparticles composed of lanthanide coordination polymers may lead to the development of new application of future luminescent materials.

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Figure captions

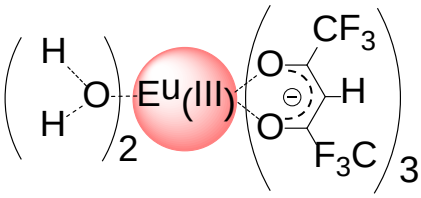
Figure1. Preparation scheme of luminescent nanoparticles composed of lanthanide coordination polymers, $[Eu(hfa)_3(dpbp)]_n$, using micelle techniques in water.

Figure2. Size distributions of a) micelle **A**, b) micelle **B**, c) mixed micelle **C**, and d) washed lanthanide coordination nanoparticles using DLS measurements. e) SEM image of washed lanthanide coordination nanoparticles.

Figure3. a) XRD patterns of lanthanide coordination nanoparticles composed of $[Eu(hfa)_3(dpbp)]_n$. b) TGA curves of nanoparticles composed of $[Eu(hfa)_3(dpbp)]_n$ in argon atmosphere at a heating rate of $1^oC\ min^{-1}$.

Figure4.a) Emission spectra of Eu(III) coordination nanoparticles composed of $[Eu(hfa)_3(dpbp)]_n$ in acetone-d_6 at room temperature. Excited at 380 nm. b) Emission decay of nanoparticles composed of $[Eu(hfa)_3(dpbp)]_n$ in acetone-d_6 at room temperature excited at 355 nm (third harmonic of a Q-switched Nd:YAG

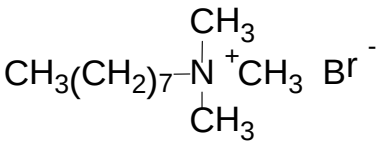
laser: fwhm = 5 ns, λ =1064 nm).



$Eu(hfa)_3 2H_2O$

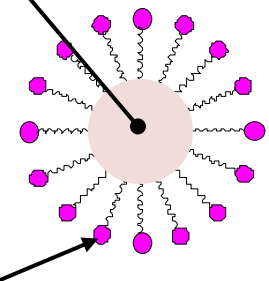
Diethyl ether

Micelle A



TMOA

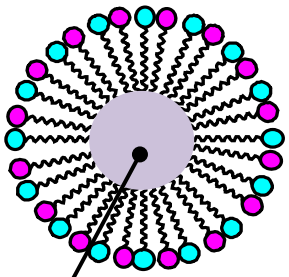
H_2O

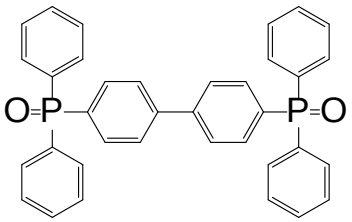


Mixing

Stirring

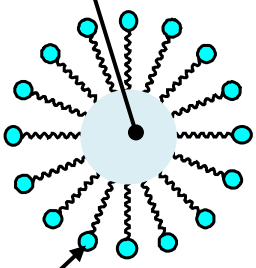
Mixed Micelle C

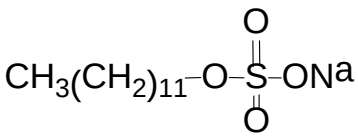




dpbp

Dichloro methane

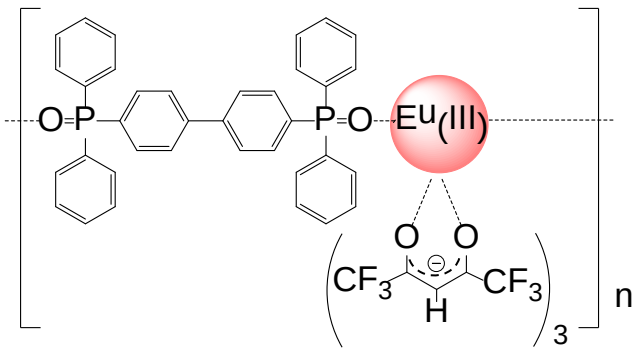




SDS

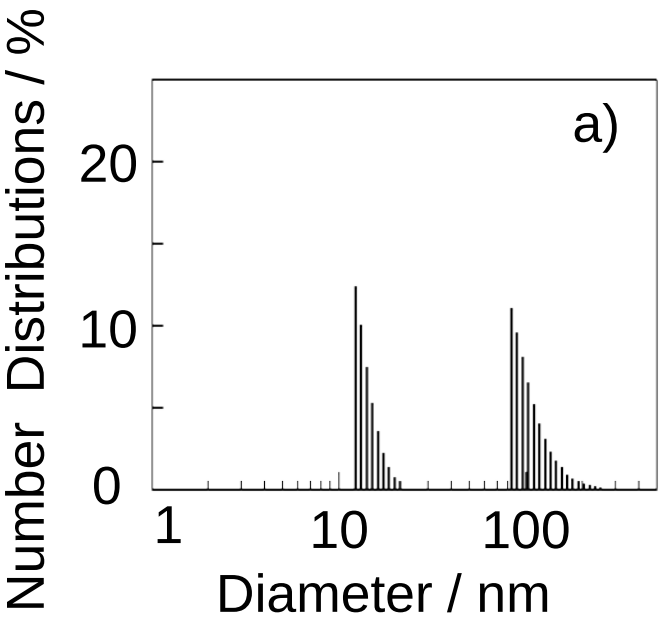
H_2O

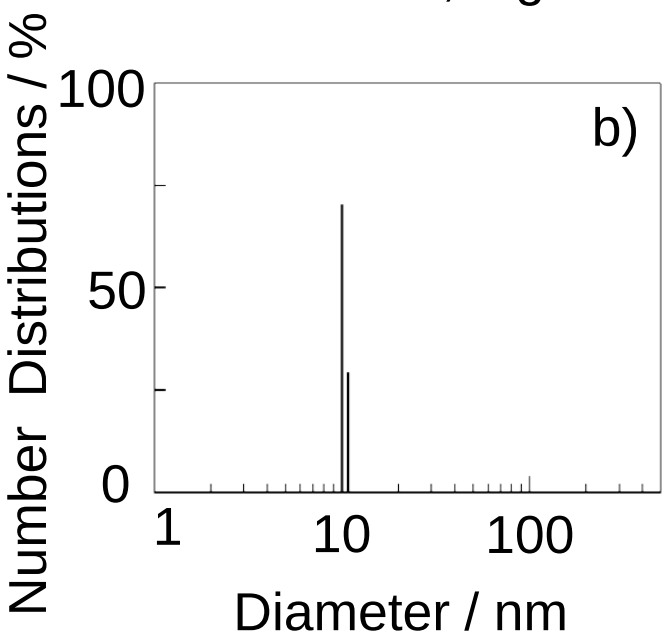
Micelle B

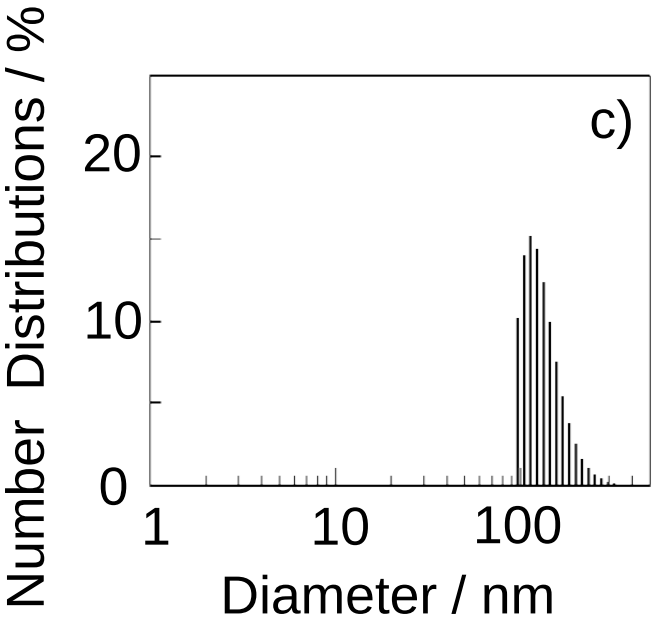


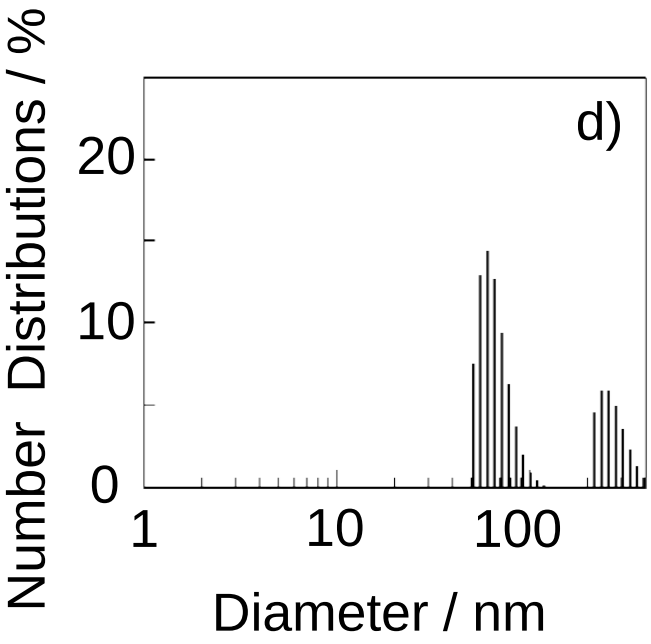
Lanthanide coordination nanoparticles

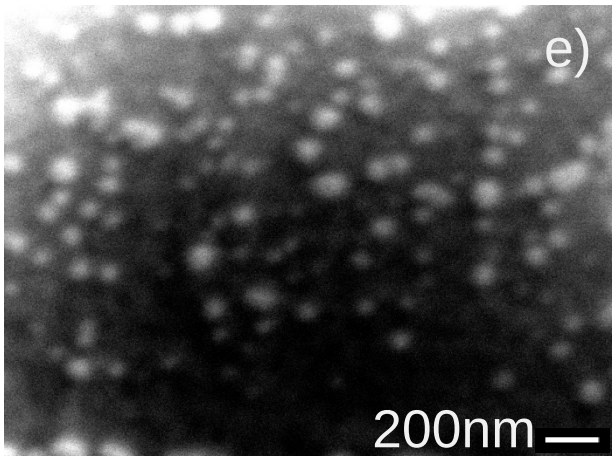
Onodera et al, Figure 2



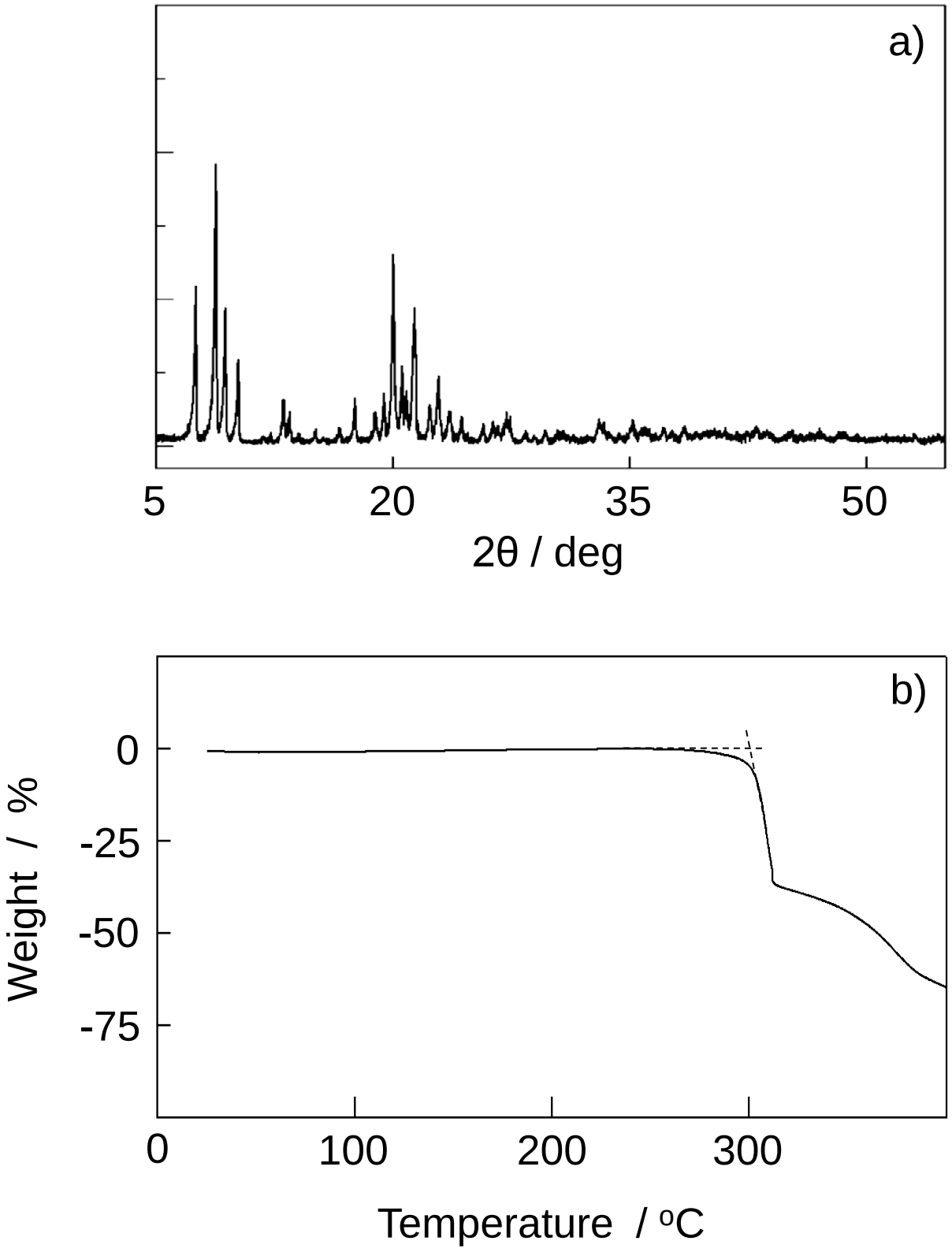
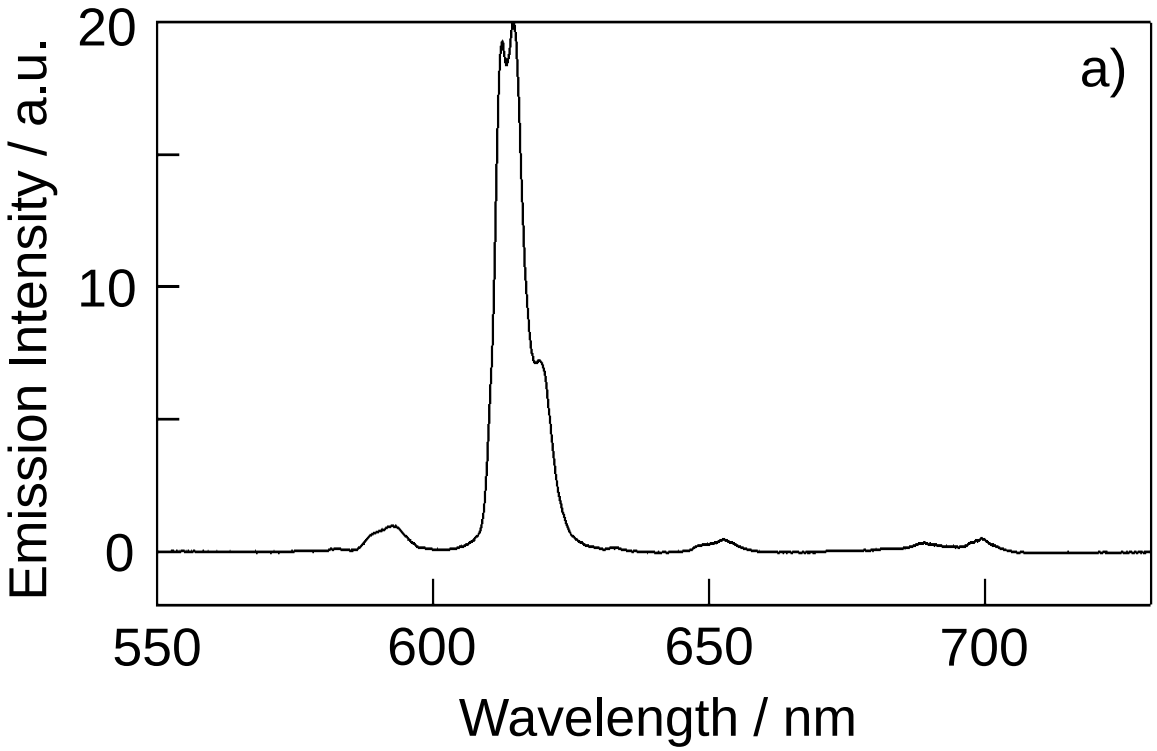
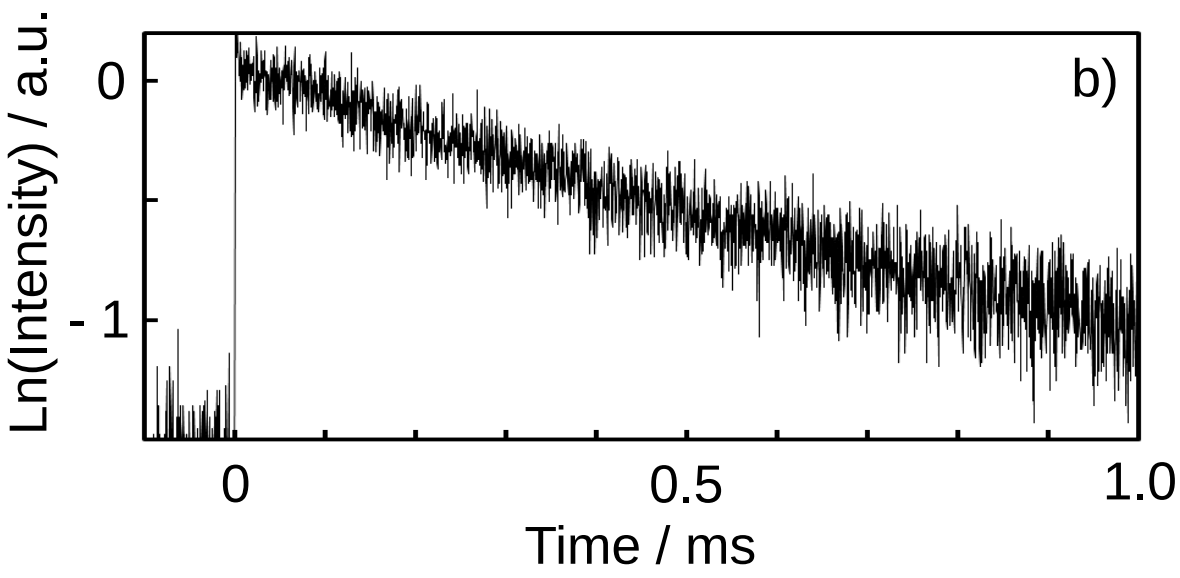








Onodera et al, Figure 3



Onodera et al, Figure 4