

Surfactant-Free Solution Synthesis of Fluorescent Platinum Subnanoclusters

Hideya KAWASAKI^{†,*}, Hiroko YAMAMOTO[†], Hiroki FUJIMORI[†], Ryuichi ARAKAWA[†],
Mitsuru INADA[‡], Yasuhiko IWASAKI[†]

[†] Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho; Suita-shi, Osaka 564-8680; Japan

[‡] Department of Pure and Applied Physics, Faculty of Engineering Science, Kansai University, 3-3-35, Yamate-cho; Suita-shi, Osaka 564-8680; Japan

E-mail: hkawa@kansai-u.ac.jp

Experimental details

Materials. H₂PtCl₆ and 2-mercaptobenzothiazole (MBT) were obtained from Wako Chemical Co. All solvents and other chemicals were reagent grade from Wako Chemical Co, and were used without further purification. Ultra pure water used throughout all experiments was purified with an Advantec RFD 250 NB system.

Preparation of Pt NCs. A solution of 150 μL of 0.1 M aqueous H₂PtCl₆ was added to 15 mL of DMF that had been preheated to 140 °C, and the DMF solution was refluxed in a 140 °C oil bath with vigorous stirring for 8 h at 1 atmosphere. After vacuum evaporation of excess solvent below 10 mHg for 3 h at 80 °C, the residue was redissolved in selected solvents and centrifuged at 14,000 rpm for 15 min. The TGA thermogram of a dried Pt NCs showed the Pt content of dried Pt clusters was estimated to be about 54 wt% from the total weight loss of about 46 % up to 500 °C.

Photophysical properties of Pt NCs. UV–visible absorption spectra were measured using a JASCO V-670 spectrometer. Fluorescence excitation and emission spectra were obtained on a JASCO FP-6200 fluorimeter.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were recorded with a Quantera SXM spectrometer (Physical Electronics, Inc.) using the monochromatic Al K α line at

1486.7 eV. The base pressure was approximately 2×10^{-8} Torr. To compensate for charging effect, binding energies were referenced to C 1s at 284.7 eV of hydrocarbon.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). MALDI-MS was conducted with an AXIMA CFR MALDI-TOF mass spectrometer. After vacuum evaporation of excess DMF solvent, Au NCs were dispersed in 15 mL of methanol, and 1.5 mmol of solid MBT powder was added to the solution, giving equivalent concentrations of MBT and Au atoms. The solution was stirred for 24 h, yielding MBT-modified Au NCs. Au clusters in 1 mL of methanol were deposited on a MALDI target plate and air-dried. The sample was irradiated by a 337 nm N₂ pulse laser. MBT absorbed the 337 nm laser light and functioned as the MALDI matrix. Results from 100 laser pulses were averaged to obtain the spectra.

In MALDI-MS, we cannot completely rule out a possibility of the fragmentation of the Pt clusters into smaller ones during the MALDI process, but the fragmentation would be considerably suppressed at the laser fluence just above the threshold for ion detection. Even at the laser fluence just above the threshold, we found that the ion peak from Pt₅(MBT)₇ was observed, and the ion peaks from Pt₄₋₆ clusters were clearly observed at higher laser fluence. Thus, it is likely that the ion peaks from Pt₄₋₆ clusters reflect the size distribution of the original sample.

Transmission electron microscopy (TEM). A drop of NCs dispersed in methanol was placed on a carbon-coated Cu grid, and TEM images were recorded with a JEOL JEM-2010F at an acceleration voltage of 200 kV.

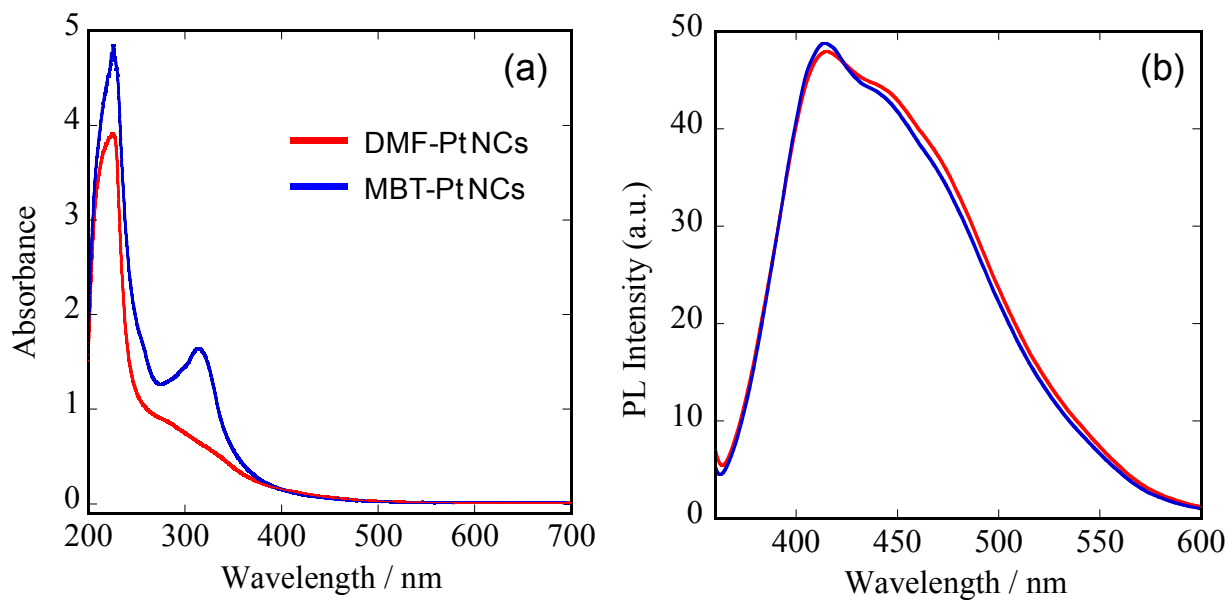


Figure S1. (a) UV-visible absorption spectra in methanol of DMF-protected Pt NCs (red), and MBA-protected Pt NCs (blue). (b) Photoluminescence emission spectra in methanol of DMF-protected Pt NCs (red) and MBA-protected Pt NCs (blue) with excitation at 350 nm.

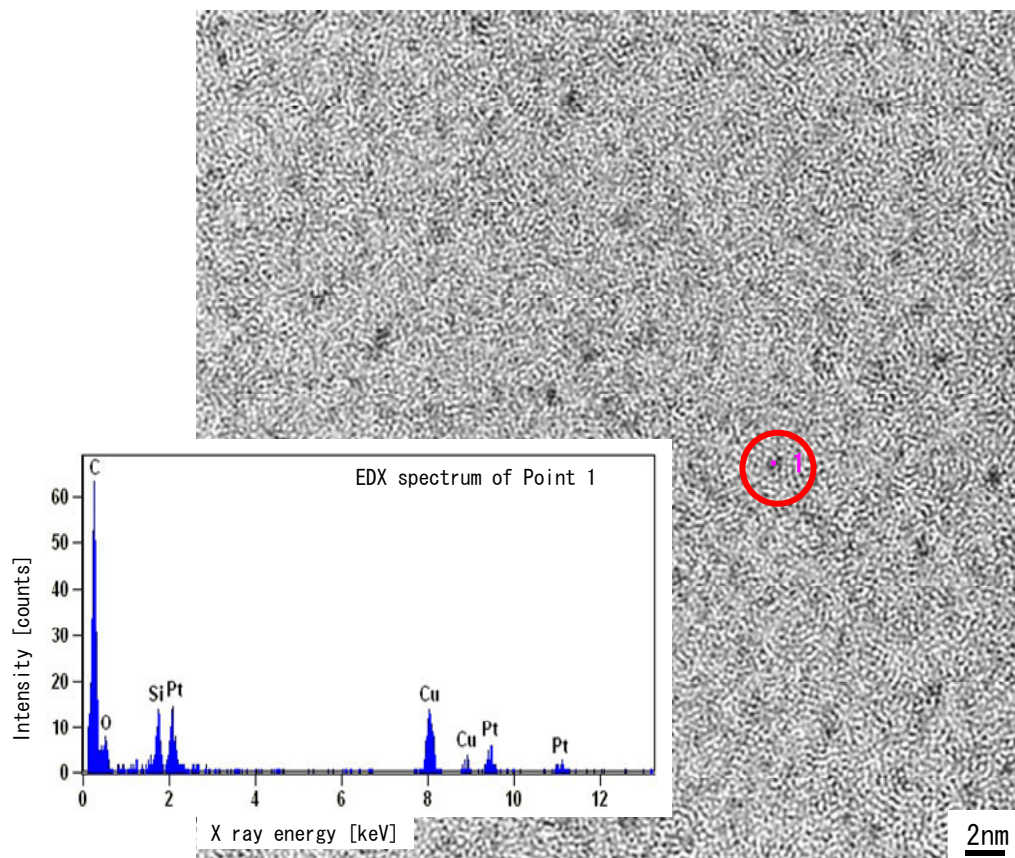


Figure S2. TEM image and the TEM-EDX spectrum recorded at point 1 in a red circle of the image of DMF-protected Pt NCs. Si and Cu peaks originated from the carbon-coated Cu grid.

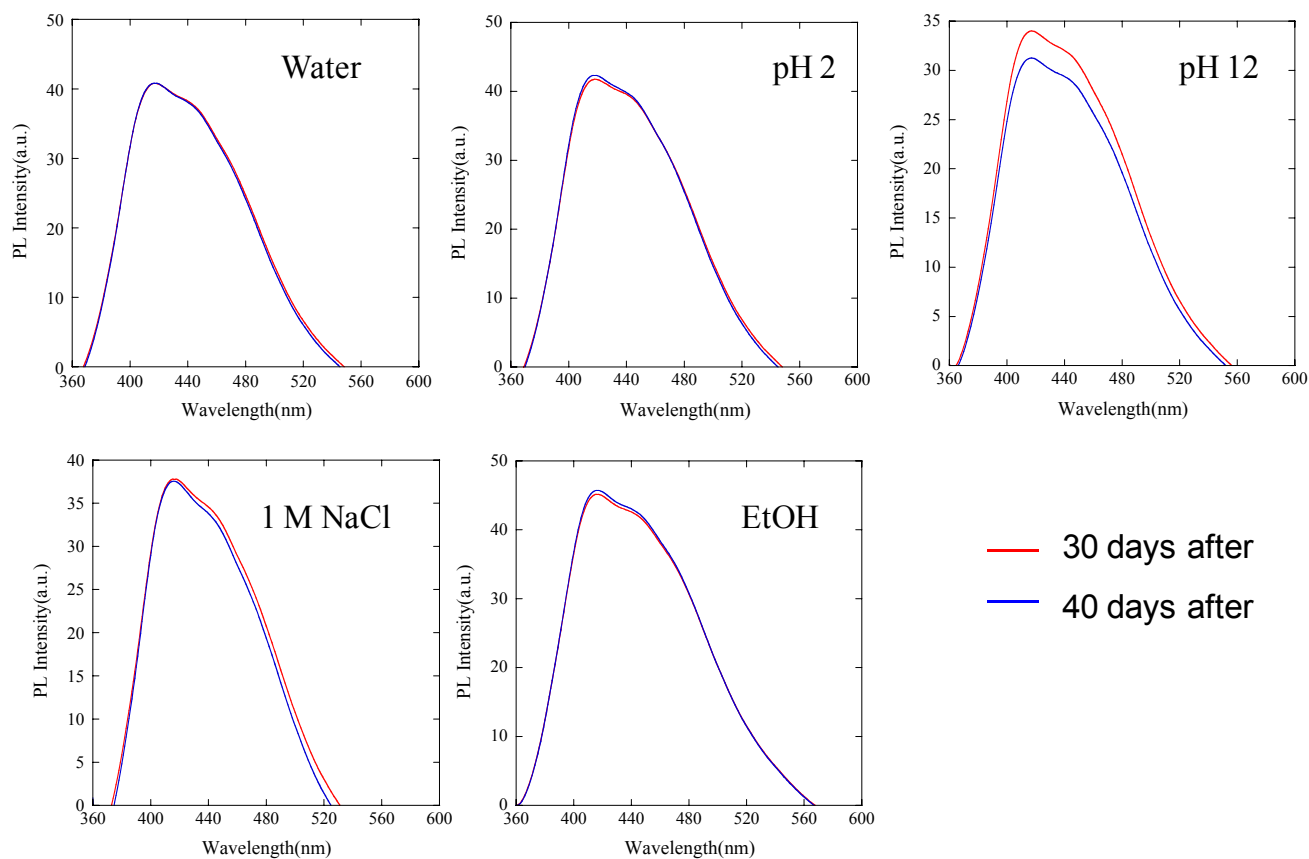


Figure S3. Photoluminescence emission spectra of DMF-protected Pt NCs in water; in aqueous solutions of acid (pH 2), alkali (pH 12), and 1 M NaCl; and in ethanol. Spectra were recorded 30 or 40 days post-synthesis at an excitation wavelength of 350 nm.