Supporting Information:

Quantitative Solid-State NMR Study on Ligand–Surface Interaction in Cysteine-capped CdSe Magic-Sized Clusters

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Contents

1. Synthesis and Solidification of CdSe-Cys

Cadmium (foil, ^{113}Cd 93.35%) and L-cysteine (^{15}N 98%) were purchased from ISOFLEX USA and Cambridge Isotope Laboratories, respectively. Selenium (powder, 99%), sodium sulfite (Na_2SO_3) (97%), sodium hydrate (NaOH) (93%), nitric acid (60–61%) and acetone (99.5%) were obtained from Wako Pure Chemicals. All chemicals were used as received.

CdSe-Cys aqueous solution was synthesized by the method of Park et al.[1,2] with some modifications. Se precursor, sodium selenosulfite (Na_2SeSO_3) solution, was prepared by stirring 50 mg of selenium powder, 290 mg of Na_2SO_3, and 12.5 ml of distilled H_2O at 950 rpm in a brown grass vial at 105°C overnight. 10 mg/ml Cd^{2+} solution was obtained by dissolving more than 50 mg of cadmium shot in nitric acid, and then 5 ml of the Cd^{2+} solution was transferred to a centrifuge tube. Cadmium hydroxide ($Cd(OH)_2$) was precipitated by adding about 10 ml of 5 M NaOH to the Cd^{2+} solution, and collected by centrifugation at 10,000 rpm for 5 min. Cd precursor, cadmium-cysteine complex solution, was produced by dissolving the $Cd(OH)_2$ in basic cysteine solution composed of 1.78 ml of 1 M L-cysteine and 8 ml of 1 M NaOH. The Cd precursor and 4.45 ml of the Se precursor cooled down to room temperature were mixed in the centrifuge tube. The reaction mixture, which molar ratio of Cd : Se : cysteine was 1 : 0.5 : 4 and pH was about 13, was pale yellow at first, and as the reaction progressed, the color became deeper. The reaction progress was monitored by UV-Vis absorption spectra. After about 24 h, the stabilization of the position and intensity of the absorption peak was observed, and then, 7.5 ml of acetone was added to the mixture to precipitate yellow CdSe-Cys. CdSe-Cys were collected by centrifugation at 10,000 rpm for 5 min, and finally obtained after vacuum drying.

2. Experimental conditions of UV-Vis

UV-Vis absorption spectrum of as-prepared CdSe-Cys aqueous solution was measured on a U-2800M double beam spectrometer (Hitachi High-Tech Science). The CdSe-Cys solution was made by diluting 20 µl of CdSe-Cys solution just before solidification in 3 ml of distilled H_2O, to avoid saturation of the spectral peak intensity.

3. Experimental conditions of solid-state NMR

All solid-state NMR experiments were performed in a 9.4 T magnet (^{1}H 400.23 MHz, ^{113}Cd 88.82 MHz, and ^{15}N 40.56 MHz) with a 3.2 mm T3 HXY triple-tuned MAS probe (Chemagnetics) on an OPENCORE spectrometer.[3] To tune ^{1}H–^{113}Cd–^{15}N triple resonance, a homemade plug-in was used for the probe. ^{15}N{^{1}H} and ^{113}Cd{^{1}H} CP/MAS spectra were acquired at spinning speeds of 10 kHz, under ^{1}H two pulse phase modulation (TPPM) decoupling[4] with radio-frequency (rf) irradiation strength of 100 kHz. The pulse sequences for ^{15}N–^{113}Cd *J*-1QF and REDOR experiments are shown in Figure S1 and S3. In our REDOR sequence, 180° pulses used in the original paper were substituted by 60°-300°-60° composite 180° pulses[5] with XY-8 phase cycling to compensate for the resonance offset caused by the broadness of ^{113}Cd peak (See Figure S4). Both experiments were done at a spinning speed of 10 kHz using a 180° pulse length of 10.6 μs for ^{15}N and ^{1}H TPPM decoupling with rf irradiation strength of 100 kHz. For ^{113}Cd, a 90° pulse length of 4 μs was used in *J*-1QF experiment, and 60° and 300° pulse lengths of 2.55 and 13.5 μs were in REDOR experiments. The chemical shifts of ^{1}H, ^{15}N, and ^{113}Cd were corrected by referencing TMS at 0 ppm, NH_4Cl at 39.3 ppm relative to NH_3 liquid,[6] and $Cd(ClO_4)_2 \cdot 6H_2O$ at 0 ppm, respectively.

4. ^{15}N–^{113}Cd *J*-1QF experiment

The *J*-1QF experiment (the pulse sequence is shown in Figure S1) allows us to observe only the signal of ^{15}N having the ^{15}N–^{113}Cd $J_{\mathrm{N–Cd}}$ interaction through a chemical bond to ^{113}Cd. In one experiment, two kinds of coherences, both of which are composed of ^{15}N signals with and without the $J_{\mathrm{N–Cd}}$ interaction, are separately created during the 2τ period by a fundamental pair of the ^{113}Cd pulse phases (φ_{31}, φ_{32}) = (x, x) and (x, −x), and detected by a receiver which phase is set as x and –x, respectively. The peak area intensities of the two acquired signals are written as

$$I_{\mathrm{N-Cd}} \cos(2\pi J_{\mathrm{N-Cd}} \tau) + I_{\mathrm{N}}$$

and

$$-I_{\mathrm{N-Cd}} - I_{\mathrm{N}},$$

where $I_{\mathrm{N–Cd}}$ is the signal with the $J_{\mathrm{N–Cd}}$ interaction and I_{N} is that without the interaction. As a result of accumulation of the two signals, only the signal $I_{\mathrm{N–Cd}}$ is obtained, whereas I_{N} is cancelled out. The observed ^{15}N signal evolves under the $J_{\mathrm{N–Cd}}$ interaction during the 2τ period, and by considering the T_2 relaxation time, the peak area intensity of the signal is described as Eq. (1) shown in the main article. The complete phase cycles actually used in our experiment to eliminate artifacts are described in the figure caption of Figure S1.

5. ^{15}N–^{113}Cd REDOR experiment

In the REDOR experiments (the pulse sequence is shown in Figure S3), two types of the experiments were conducted with and without the irradiations of ^{113}Cd composite 180° pulses for each dipolar dephasing time, and area intensities of ^{15}N normal spin–echo (S_0) and reduced (S_r) spectra were acquired, respectively. Experimental REDOR fractions were calculated as $\Delta S/S_0 = (S_0 - S_r)/S_0$. When a ^{15}N peak is composed of two sites, one of which is close to the ^{113}Cd and the other is far from, ΔS of the ^{15}N peak can be written as

$$\Delta S = f\Delta S^{\text{close}} + (1-f)\Delta S^{\text{far}}$$

where f is the ratio of the ^{15}N close to the ^{113}Cd. By assuming that ^{15}N–^{113}Cd dipolar interaction of the ^{15}N far from the ^{113}Cd is negligible, we can assume that ΔS^{far} is to be ~0. Therefore, the experimental REDOR fraction can be expressed as

$$\frac{\Delta S}{S_0} \sim f\frac{\Delta S^{\text{close}}}{S_0}.$$

In our work, the ratio f is estimated to be ~0.5 from the intensities of the experimental fractions. The analytical expression of theoretical REDOR function, which consists of Bessel functions of the first kind,[7] should also be scaled by the ratio f (~0.5) and given as

$$\frac{\Delta S}{S_0} = f\left[1 - \frac{\sqrt{2}\pi}{4}J_{1/4}\left(\sqrt{2}D\tau_{\text{d}}\right)J_{-1/4}\left(\sqrt{2}D\tau_{\text{d}}\right)\right],$$

where D is the ^{15}N–^{113}Cd dipolar coupling constant (Hz) and τ_{d} is the dipolar dephasing time (ms). The fractions are referred to the theoretical functions calculated by using D as an adjustable parameter, and the best fitting value of D is determined. The ^{15}N–^{113}Cd internuclear distance r is finally obtained from an equation of the parameter $D = \gamma_{\text{N}}\gamma_{\text{Cd}}\hbar/2\pi r^3$, where γ_{N} and γ_{Cd} are gyromagnetic ratios of ^{15}N and ^{113}Cd, respectively.

6. Figures

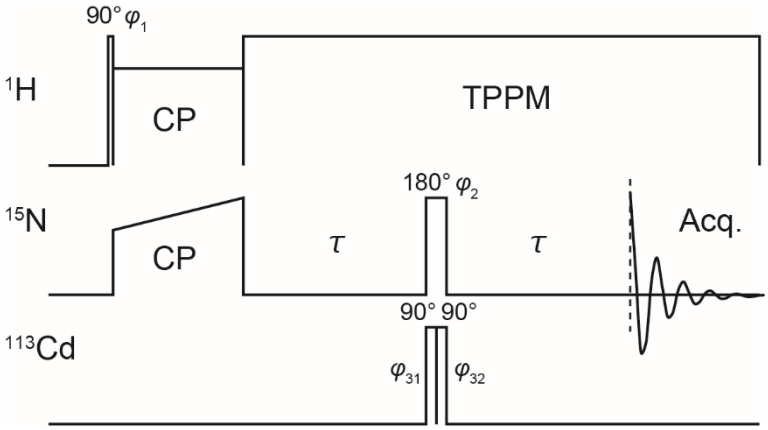

Figure S1. Pulse sequence for ^{15}N–^{113}Cd *J*-1QF experiment. Only the ^{15}N signal having the $J_{N–Cd}$ interaction can be acquired by suitably setting the phase cycling of the pulses and a receiver as follows: φ_1 = y, −y; φ_2 = x, x, x, x, y, y, y, y, −x, −x, −x, −x, −y, −y, −y, −y; φ_{31} = x; φ_{32} = x, x, −x, −x; receiver = x, −x, −x, x, −x, x, x, −x.

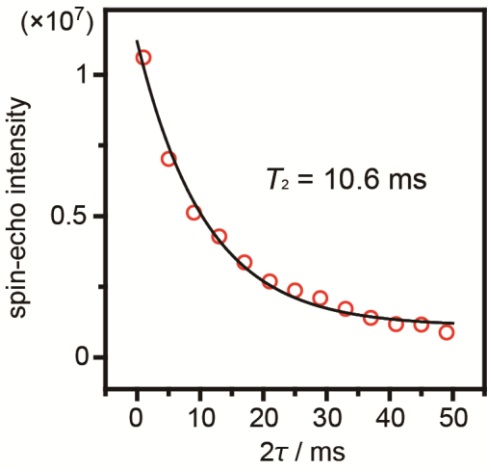

Figure S2. Plot of ^{15}N major peak intensities of CdSe-Cys in ^{15}N spin-echo experiments. The data were fitted by $I_{full}\exp(-2\tau/T_2)$ as described in the main article.

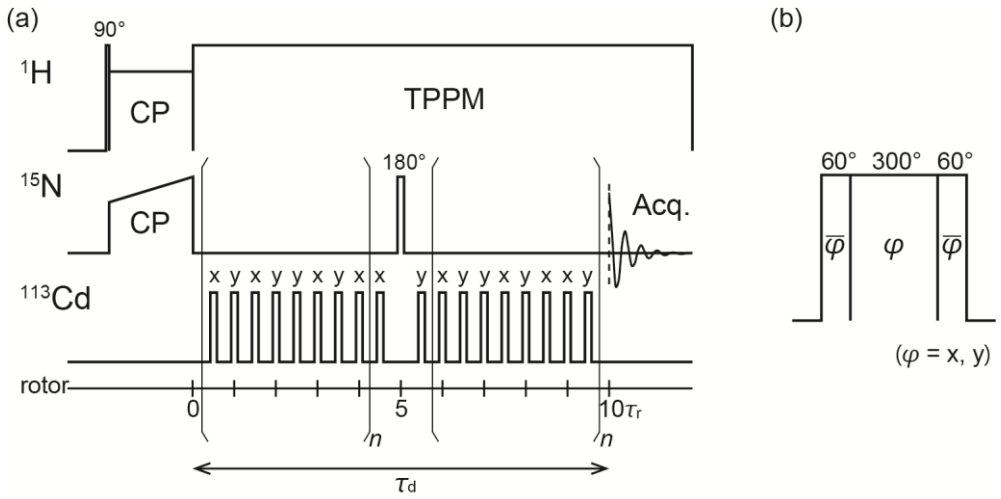

Figure S3. (a) Pulse sequence for ^{15}N–^{113}Cd REDOR experiment and (b) 60°-300°-60° composite 180° pulse applied to ^{113}Cd pulses. In this sequence, the dipolar dephasing time (τ_d) is given as $(8n - 2)\tau_r$, where the number n means the loop times of the composite 180° pulse blocks and τ_r is the MAS rotor period.

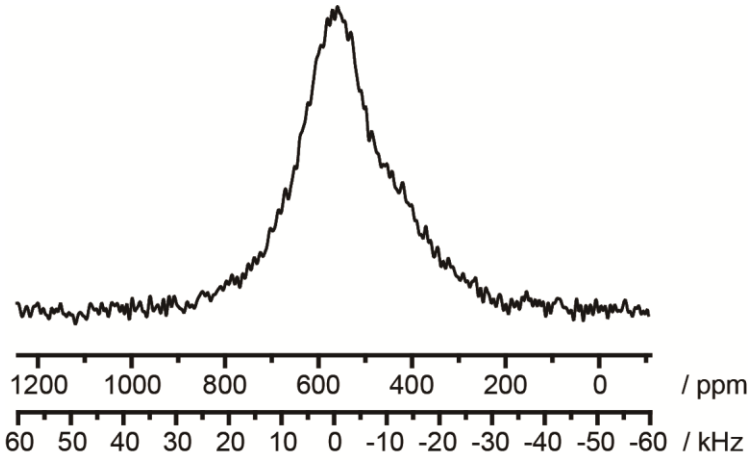

Figure S4. ^{113}Cd CP/MAS NMR spectrum of CdSe-Cys.

7. References

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