Supplementary Information for

**Giant Zeeman splitting in nucleation-controlled doped CdSe:Mn\textsuperscript{2+} quantum nanoribbons**

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**Characterization.** The synthesized nanoribbons were characterized by low- and high-resolution transmission electron microscopy (TEM) and X-ray diffraction (XRD). The low-magnification TEM images were obtained using a JEOL EM-2010 microscope. The high-resolution TEM images were obtained using a JEOL EM-3000F microscope. The powder X-ray diffraction patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode and a Cu KR radiation source (\(\lambda = 0.15418 \text{ nm}\)), and the Bragg peaks were fitted to Pearson-VII functions to calculate the lattice constants. X-ray absorbance spectroscopy (XAS) was performed at the Dragon beamline (11A) of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. Extended X-ray absorption fine structure (EXAFS) spectroscopy was performed at 7C1
Beamline of Pohang Accelerator Laboratory (PAL) in Korea. The EXAFS spectra were analyzed using the ATHENA program, and were modeled theoretically using ARTEMIS.

The optical properties of the nanoribbons were characterized by optical absorption and fluorescence spectroscopy, using a JASCO V-550 UV-VIS spectrometer and FP-6500 spectrofluorometer, respectively. The electron paramagnetic resonance (EPR) spectra were obtained at 77 K using a Bruker EMX 300 Electron Paramagnetic Resonance spectrometer at the microwave frequency of 9.5 GHz with 0.01 kHz resolution. Inductively-coupled plasma-atomic emission spectra (ICP-AES) were measured using Shimadzu ICPS-1000 IV ICP-AES spectrometer. Before the EPR and ICP-AES characterizations, all the samples were washed 5 times with pyridine to remove any excess manganese ions on the nanoribbon surface. Time-resolved luminescence kinetic measurements were carried out in an Edinburgh FLS 920 time correlated single photon counting spectrometer (TCSPC), with nanosecond flash Xenon lamp as excitation source, Czerny-Turner monochromator, and MCP-PMT detector.

**Synthesis of Mn$^{2+}$ doped (CdSe)$_{13}$ clusters.** The (CdSe)$_{13}$:Mn$^{2+}$ clusters were synthesized from the reaction of CdCl$_2$ and MnCl$_2$ octylammonium selenocarbamate in octylamine at 30 °C. Octylamine solution of CdCl$_2$ and MnCl$_2$ was prepared by heating 10 mL of octylamine containing 1.5 mmol (0.275 g) of CdCl$_2$ and 0.0075 mmol (0.0094 g) of MnCl$_2$ at 120 °C for 2 hr. At this stage, octylamine and CdCl$_2$ reacted to form a
mixture of CdCl₂(octylamine)₂ and MnCl₂(octylamine)₂ complexes. Octylammonium selenocarbamate was prepared by bubbling CO gas into 5 mL of octylamine containing Se powder (0.355 g, 4.5 mmol), with vigorous stirring for 2 hr at room temperature. During this process, the solution color was gradually changed to red brown, finally becoming turbid white. The as-prepared octylammonium selenocarbamate in octylamine was injected into the cadmium-octylamine complex solution at room temperature, instantly generating a transparent light yellow solution, which is an indication of (CdSe)₃₄ clusters formation. This solution was aged at room temperature for 12 hours. During the aging process, the solution colors turns from light yellow to turbid white solution of (CdSe)₁₃:Mn²⁺ clusters.

**First principles quantum mechanical calculations.** The calculations were performed on the basis of spin polarized density functional theory (DFT) within the generalized gradient approximation (GGA-PW91), as implemented in the Vienna Ab-initio Simulation Package (VASP). The projector-augmented wave (PAW) method with a plane wave basis set was employed to describe the interaction between the core and the valence electrons. An energy cutoff of 300 eV was applied for the plane wave expansion of electronic eigenfunctions. All atoms were fully relaxed using the conjugate gradient method until residual forces on constituent atoms became smaller than 3×10⁻² eV/Å. The gamma point was used for the Brillouin zone sampling. The spin interpolation formula proposed by Vosko et al. was used to calculate magnetic moments.
and magnetic energies.

**Magneto-Optical Spectroscopy.** The magnitude of the measured MCD is expressed as

\[
MCD = \frac{T^+(E) - T^-(E)}{T^+(E) + T^-(E)},
\]

(1)

where \(T^+(E)\) and \(T^-(E)\) are, respectively, transmission intensities of right (\(\sigma^+\)) and left (\(\sigma^-\)) circularly polarized light. When an external magnetic field is present, the exciton in the CdSe:Mn\(^{2+}\) quantum nanoribbon undergoes a Zeeman splitting \(\Delta E\), and the difference between the \(\sigma^+\) and the \(\sigma^-\) absorptions gives rise to the MCD signal at energies near the excitonic transition. The relation between MCD signal and the Zeeman splitting (\(\Delta E\)) can be expressed as\(^{S6}\).

\[
MCD = \frac{d[\ln T(E)] \Delta E}{dE} / 2,
\]

(2)

where \(T(E)\) is the transmission intensity at energy \(E\).

**Calculation of s-d exchange constant.** In order to determine the effective concentration of Mn ions in our samples we performed numerical simulations of the spin pairing of neighboring Mn ions utilizing a random distribution of Mn in the nano-ribbon geometry (i.e., 1.4nm×30nm×200nm). In our simulations we followed the procedure developed for quantum wells by Fatah *et al.*\(^{S7}\) This simulation takes the reduced number of magnetic neighbors at the surface into account. However, our model does not account for the statistics of
possible Mn clusters at the surface. The saturation value of the excitonic Zeeman splitting in DMS materials can be described as 

\[ \Delta E_{\text{Zeeman}} = (3g_h-g_e)\mu_B H + x\langle S_z \rangle N_0(\alpha - \beta), \]

where \((3g_h-g_e)\mu_B H\) is the intrinsic excitonic Zeeman splitting, shown to be of the order of 0.1 meV/T in CdSe nanocrystal\(^\text{S8}\), \(x\) is the effective Mn\(^{2+}\) concentration, \(\langle S_z \rangle\) is the spin expectation value of the magnetic ions in the direction of the applied magnetic field (-5/2 for Mn\(^{2+}\) ions), \(N_0\alpha\) is the s-d exchange coupling between the conduction band carriers and magnetic ions, and \(N_0\beta\) is the p-d exchange coupling between the valence band carriers and magnetic ions. In our calculations we took the p-d exchange constant as 0.7 of its value in bulk materials for wurtzite CdSe:Mn\(^{2+}\) based on theoretical calculation of Bhattacharjee\(^\text{S9}\). \(N_0\beta = -1.11 \text{ eV} \times 0.7 = -0.78 \text{ eV},\) since p-d exchange interactions do not change significantly, being dominated by the kinetic exchange process.

**Supplementary Information Text**

The MCD spectra taken at \(B = 5 \text{ T}\) and \(T = 1.8 \text{ K}\) for a series of samples with different Mn concentration (Fig. S7) show that the position of MCD peaks does not depend on Mn concentration and falls for all samples within narrow energy range (i.e. 2.85eV ±30 meV), much smaller than the width of the MCD peak. Since the MCD peak should be centered at the energy gap or at excitonic transition, and the exciton energy is determined entirely by quantum confinement, we attribute the narrow energy range of the MCD peak position to the highly uniform size of the quantum nanoribbons for the entire series of Mn concentration.
References


Figure S1. a, X-ray diffraction pattern of CdSe:Mn$^{2+}$ quantum nanoribbons. The XRD pattern verifies that the CdSe:Mn$^{2+}$ quantum nanoribbons have a wurtzite crystal structure. b, The SAED pattern of single CdSe:Mn$^{2+}$ quantum nanoribbons taken along the width direction of CdSe:Mn$^{2+}$ quantum nanoribbons. c, A simulated SAED image of the (1120) plane in a wurtzite crystal.

Figure S2. Comparison of absorbance (black curve) and PLE spectrum (blue curve) corresponding to the 580 nm emission of CdSe:Mn$^{2+}$ quantum nanoribbons.
Figure S3. Comparison of the Mn K-edge EXAFS spectra with theoretically modeled α-MnSe (a) and Mn crystal structures (b). The comparison of Se K-edge EXAFS spectrum with theoretically modeled α-MnSe crystal structure (c). Mn K-edge (d) and Se K-edge (e) EXAFS spectra for various Mn$^{2+}$ concentrations within the CdSe: Mn$^{2+}$ quantum nanoribbons.
Figure S4. Calibration of ICP-AES result by EDS (energy dispersion spectrum). The result indicates the Mn$^{2+}$ concentration incorporated inside the CdSe host is of the same order of the initial MnCl$_2$ concentration used in the reaction. We used the ICP-AES result for the interpretation of our data, as ICP-AES provides a quantitatively more reliable data than EDS. The error bars represent standard deviations.
Figure S5. Photoluminescence spectrum of (CdSe)$_{34}$ clusters (blue) and MnCl$_2$-reacted (CdSe)$_{34}$ clusters (red) (a), (CdSe)$_{13}$ clusters (blue) and MnCl$_2$-reacted (CdSe)$_{13}$ clusters (red) (b). The precipitates of pure (CdSe)$_{13}$ clusters (left) and MnCl$_2$-reacted (CdSe)$_{13}$ clusters (right) (c). As the (CdSe)$_{13}$ clusters absorb only UV light, the precipitates show white color. However, the Mn-incorporated (CdSe)$_{13}$ clusters show bright orange luminescence (d).
<table>
<thead>
<tr>
<th>Position</th>
<th>$\Delta E$ [eV]</th>
<th>Position</th>
<th>$\Delta E$ [eV]/Mn</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Anti-ferro ($\uparrow\downarrow$)</td>
</tr>
<tr>
<td>A 0.17</td>
<td>C1 + A 0.01</td>
<td>[= (0.04 - 0.02) / 2]</td>
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<tr>
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<td>[= (0.09 + 0.07) / 2]</td>
<td>0.12 [= (0.04 + 0.20) / 2]</td>
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\[ \Delta E/Mn = \frac{E[Cd_{13-n}Mn_nSe_{13}] + n \times E[CdCl_2] - E[(CdSe)_{13}] - n \times E[MnCl_2]}{n} \]

**Figure S6.** Summary of the first principle quantum mechanical calculations of the cation exchange reactions between Mn$^{2+}$ ions and Cd$^{2+}$ in the magic-sized clusters (CdSe)$_{13}$. 
**Figure S7.** a-e, Synthesis and characterization of CdS:Mn$^{2+}$ quantum nanoribbons. TEM images of CdS:Mn$^{2+}$ quantum nanoribbons (a), (b). XRD (c), optical absorption and PL (d), and the EPR spectra (e) obtained on the CdS:Mn$^{2+}$ quantum nanoribbons. The photoluminescence at 580 nm (d) and the hyperfine splitting of 6.71 mT (e) indicate that Mn$^{2+}$ ions are doped into the CdS quantum nanoribbons.$^{10}$
Figure S8. MCD spectra of CdSe:Mn$^{2+}$ quantum nanoribbons for various Mn concentrations obtained at $T = 1.8$ K at $B = 5.0$ Tesla.
Figure S9. Calibration of the plot of Zeeman splitting vs. effective Mn$^{2+}$ concentration used to obtain the $s$-$d$ exchange constant. Note that the linear fit does not go through zero, most likely due to possible uncertainty in evaluating the effective Mn concentrations.