Route to the Smallest Doped Semiconductor: Mn^{2+} Doped $(CdSe)_{13}$ Clusters

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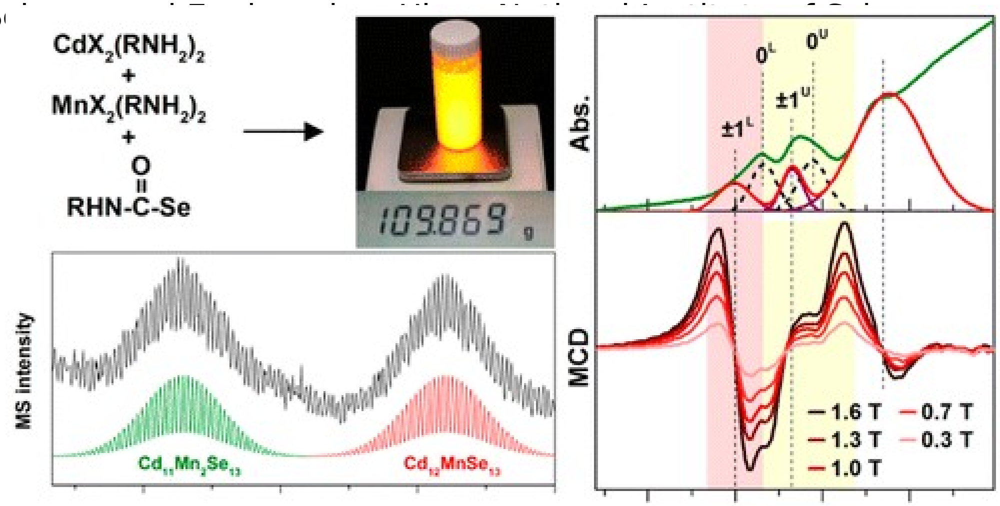

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Introduction

- Synthesis of semiconductor nanocrystals (NCs) has been rapidly developed from controlling the size and shape to designing various multicomponent heterostructures.

- Doping semiconductor NCs with magnetic transition metals have attracted substantial interests to obtain diluted magnetic semiconductor (DMS) NCs.

- Spin exchange interaction between the dopants and the charge carriers of the host in these NCs leads to unique correlated electronic and magnetic properties such as giant magneto-optical response.

- Despite the progress on the doping of semiconductor NCs, the study of doped semiconductor NCs is usually limited to NCs larger than 2 nm.

- Doping of NCs is known to be induced by the adsorption of impurities on the surface of growing NCs.

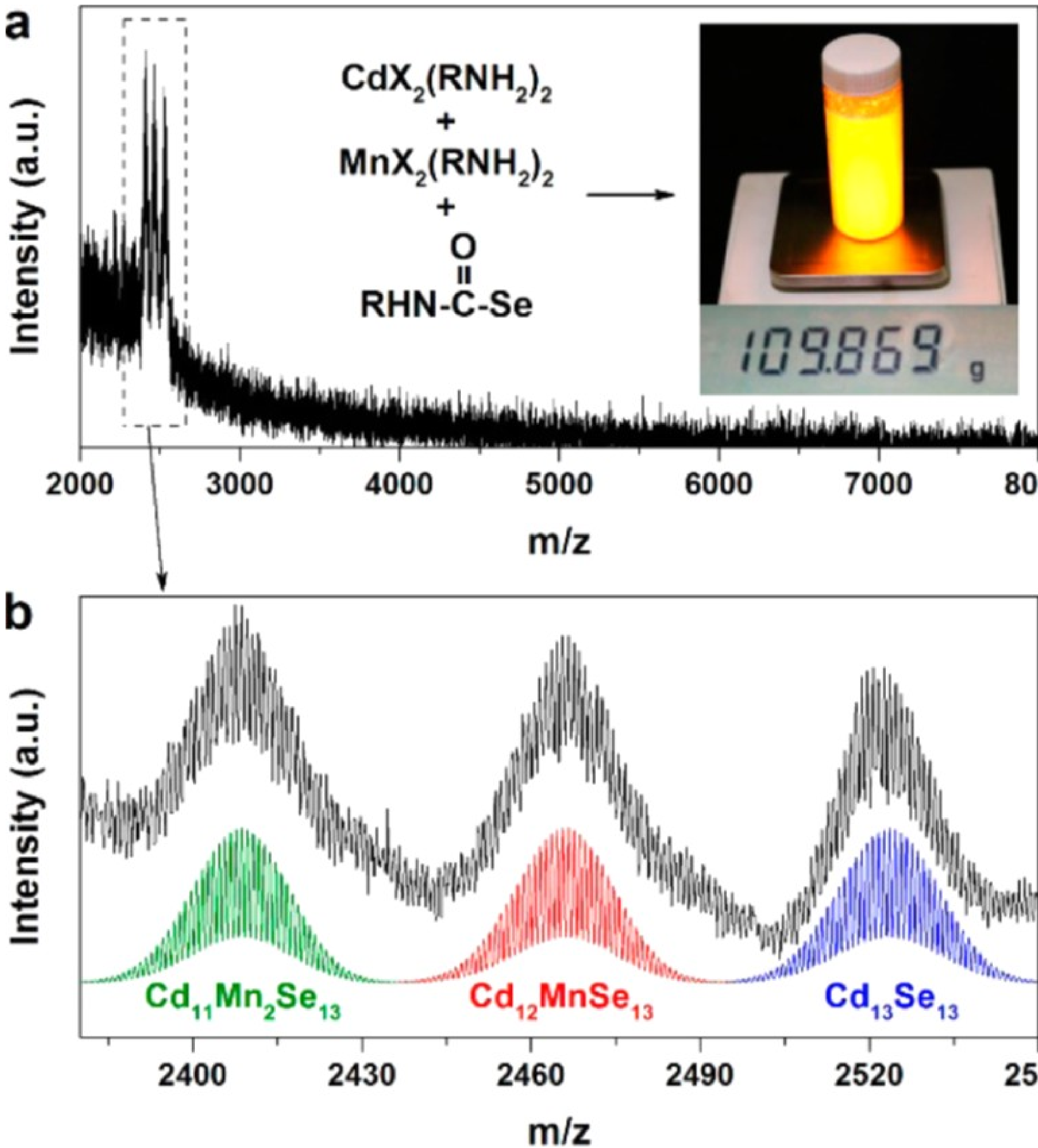
In this paper

- Herein we report on the synthesis and characterization of the smallest doped semiconductor, Mn^{2+}-doped $(CdSe)_{13}$ clusters.

$CdCl_2$ + $MnCl_2$ + n-octylamine —(Ar, 120˚C, 2h)→ MCl_2(n-octylamine)$_2$ (M= Cd, Mn) (1)

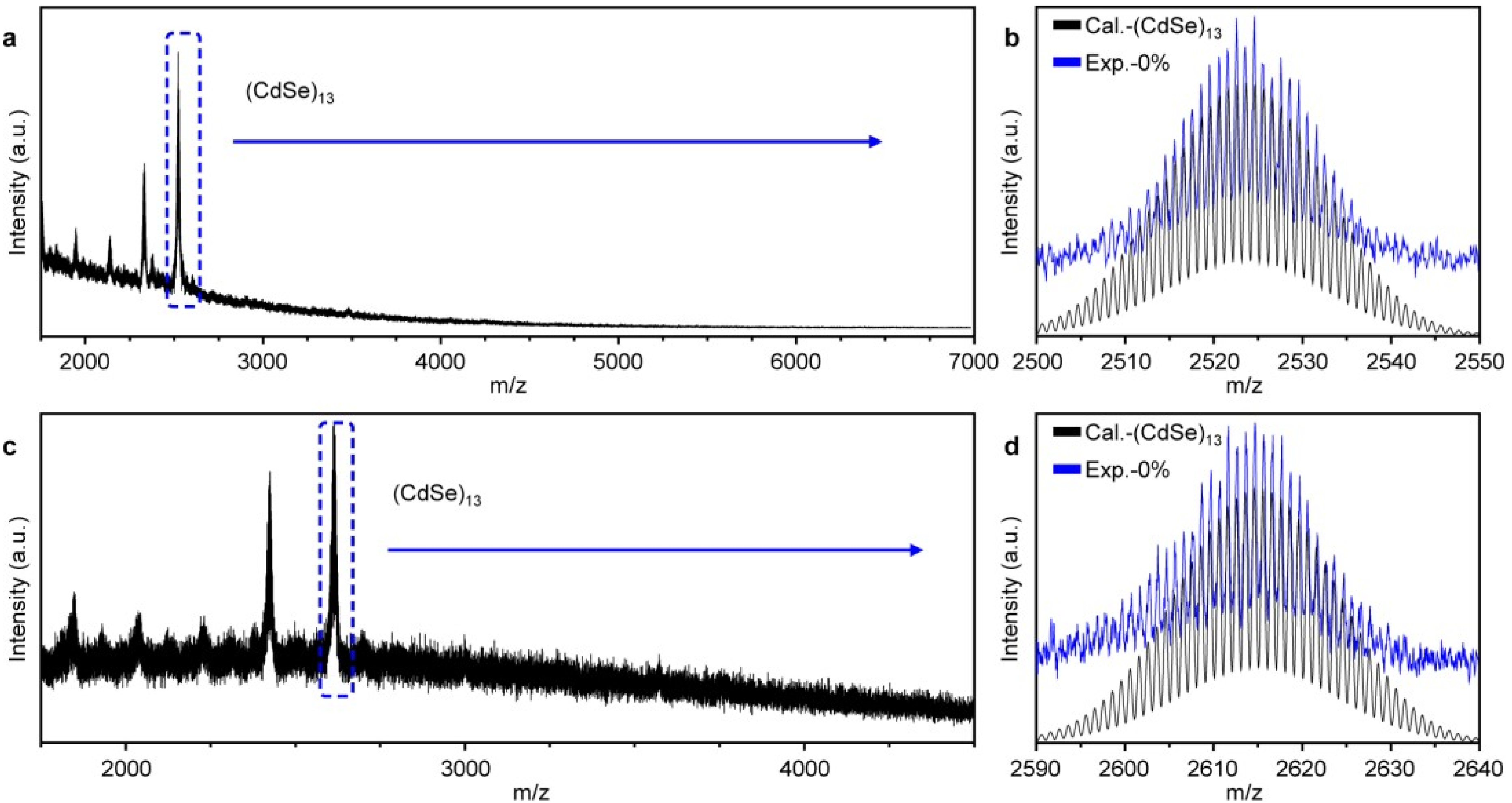
n-octylamine + Se —(CO, RT, 1 h)→ RHN-CO-Se (octylammonium selenocarbamate) (2)

1+2 —(RT, 40 hr)→ cluster



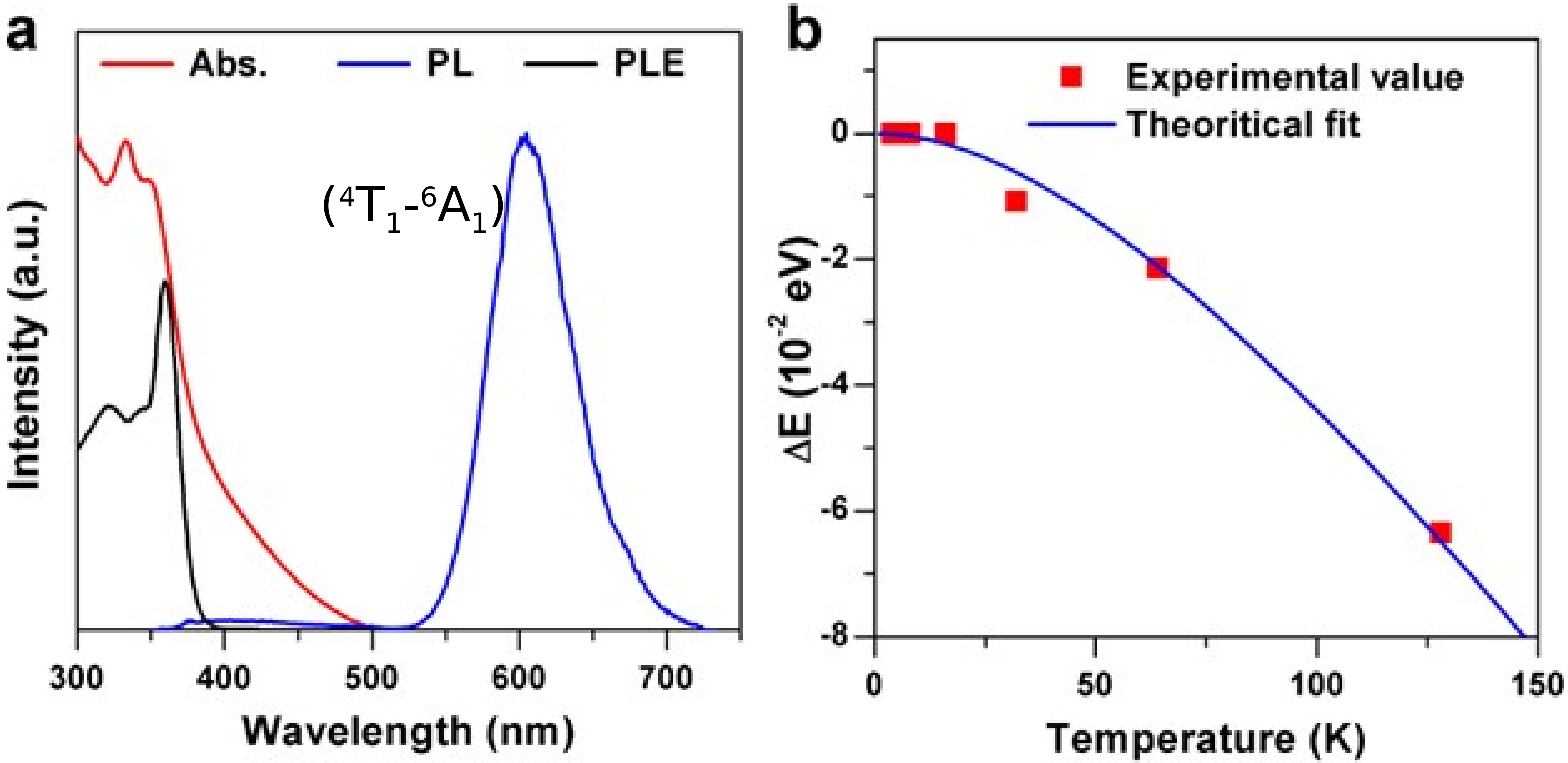
(a) Mass spectrum of Mn^{2+}-doped $(CdSe)_{13}$ clusters ionized with Cl^-. The average doping concentration of the clusters is 7%. The inset shows the amount of the product from a single batch large-scale synthesis.

(b) High-resolution mass spectrum of the main peaks indicated with the dashed box in panel a. Below the measured data, calculated isotopic distributions of $Cd_{13}Se_{13}$ (blue), $Cd_{12}MnSe_{13}$ (red), and $Cd_{11}Mn_2Se_{13}$ (green) are shown for comparison.

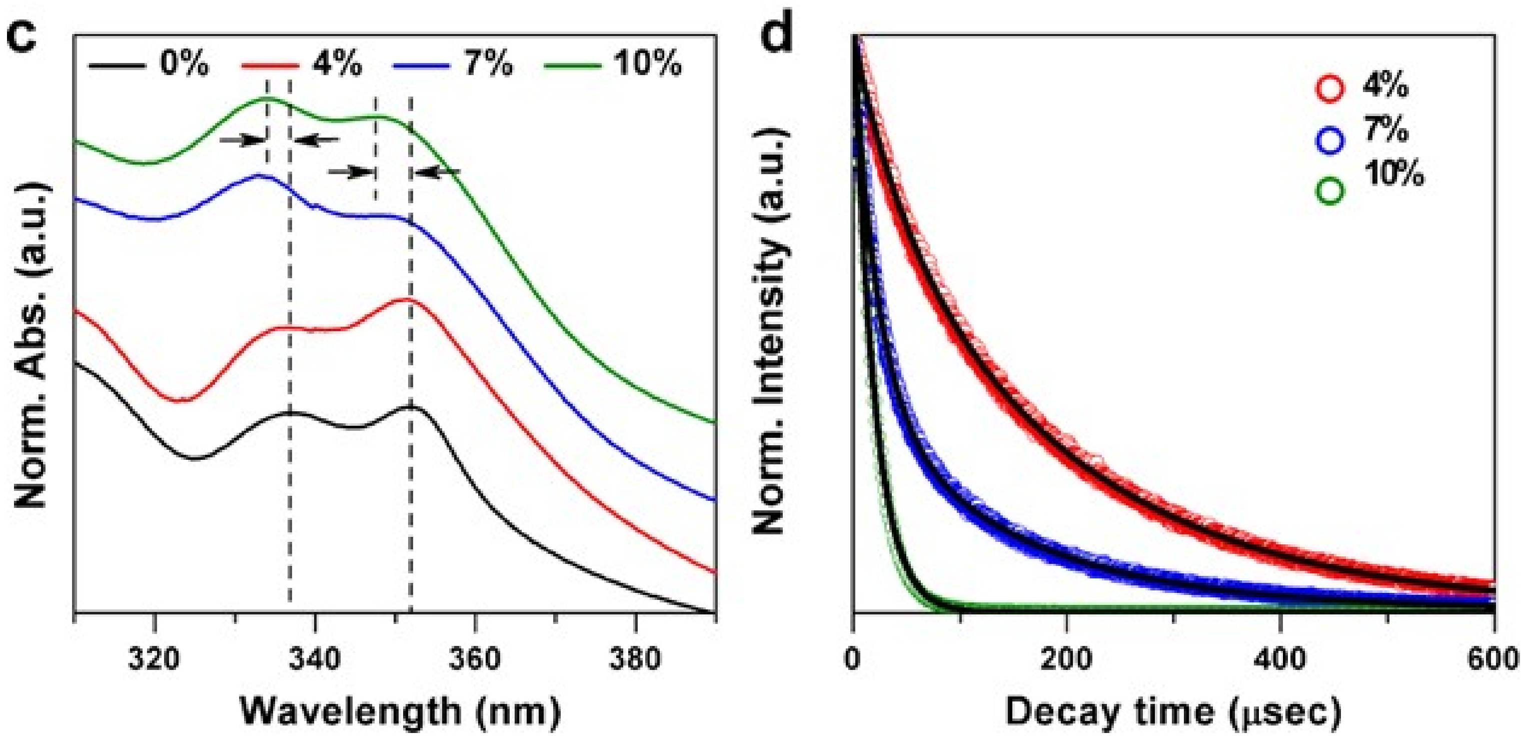


a) LDI-TOF MS spectrum of undoped $(CdSe)_{13}$ clusters ionized by chlorine anions. (b) The expansion around the main peak in panel a (blue rectangle) in isotopic resolution. (c) LDI-TOF MS spectrum of undoped $(CdSe)_{13}$ clusters ionized by iodine anions. (d) The expansion around the main peak in panel c (blue rectangle) in isotopic resolution.

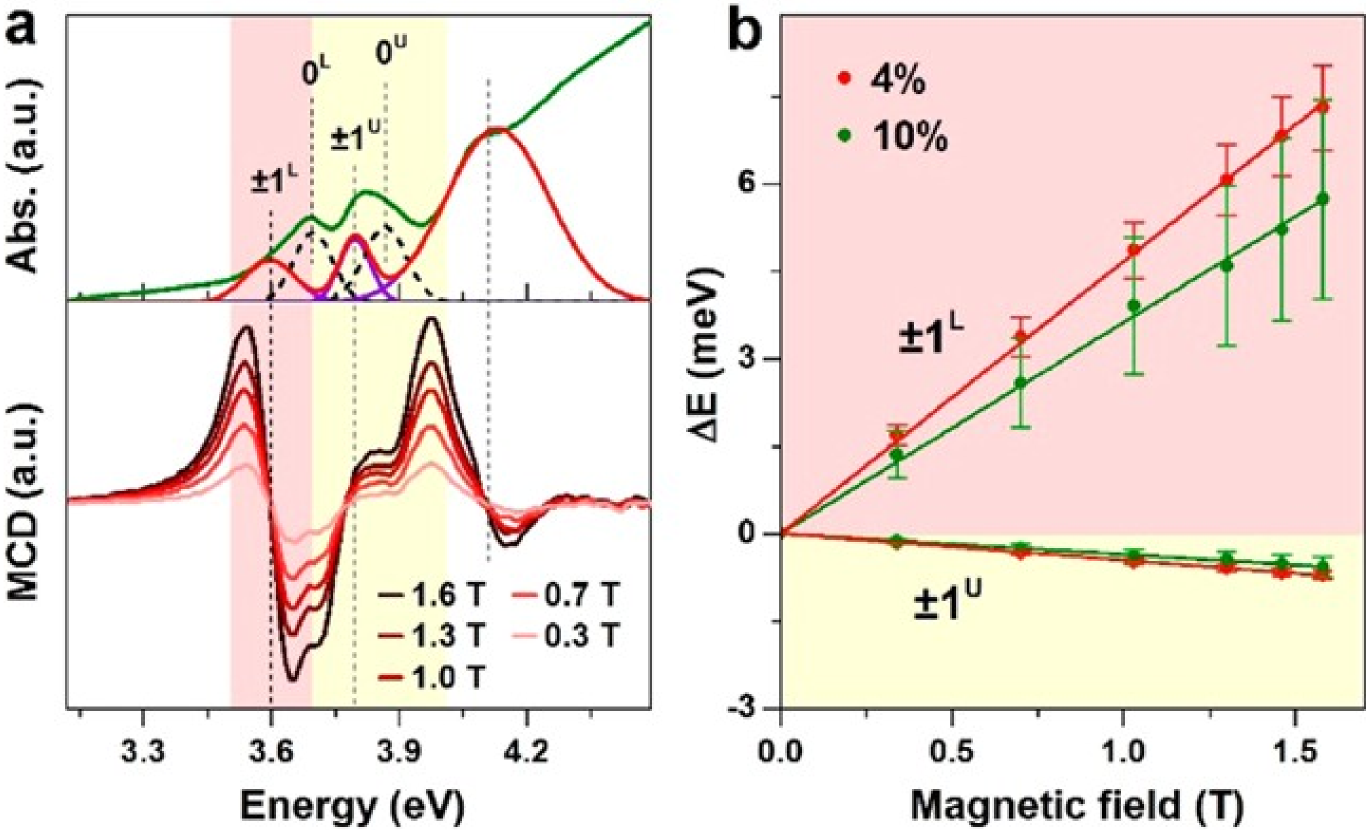
❖ Peaks from other CdSe clusters, such as $(CdSe)_{34}$ or $(CdSe)_{19}$ are not observed, demonstrating the high purity of the $(CdSe)_{13}$ clusters. Minor peaks result from the fragmentation by laser.



Optical properties of Mn^{2+}-doped $(CdSe)_{13}$ clusters. (a) Spectra of absorption, PL, and PLE (detected at 600 nm) from
as-synthesized (n-octylamine capped) 7% Mn^{2+}-doped $(CdSe)_{13}$ clusters. (b) Energy shift of the absorption edge of Mn^{2+}-doped $(CdSe)_{13}$ clusters as a function of temperature. The theoretical fitting curve is calculated by using the Varshni law with the parameters $\alpha = 11 \times 10^{-4}$ eV K^{-1} and $\beta = 150$ K.

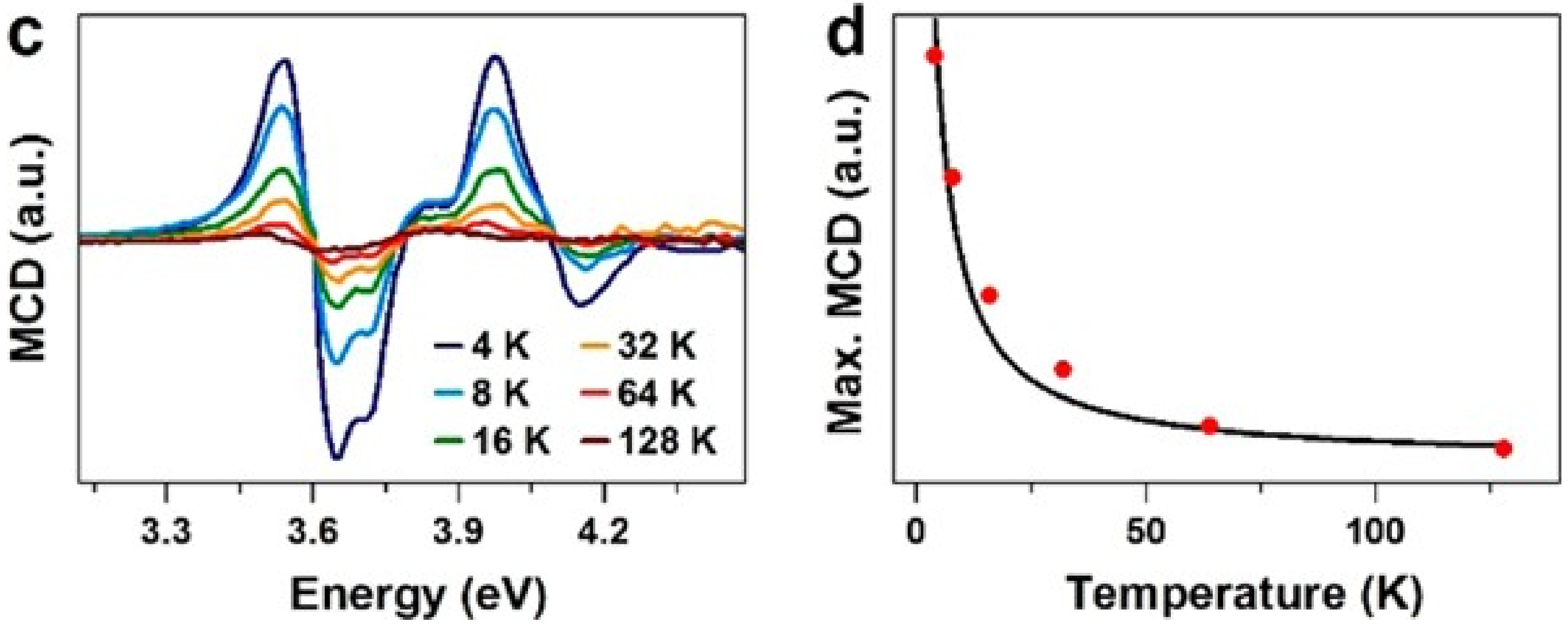


(c) Absorption spectra of $(CdSe)_{13}$ clusters with various doping concentrations. The arrows indicate the shift of the absorption peak positions. (d) Time-resolved luminescence decay at 600 nm from Mn^{2+}-$(CdSe)_{13}$ clusters with different doping concentrations. Decay data are overlapped with the corresponding fitting curve (black).



Magneto-optical properties of Mn^{2+}-doped $(CdSe)_{13}$ clusters. (a) Optical absorption (upper) and magnetic field-dependent MCD (lower) spectra of 4% Mn^{2+}-doped clusters at 4.2 K. In the upper panel, green, violet, and black dashed lines indicate measured data, magnetooptically active, and inactive peaks, respectively. The red curve is the summation of the magneto-optically active transitions. (b) Giant Zeeman splittings extracted from 4% (red) and 10% (green) Mn^{2+}- doped clusters

- Slightly lower Zeeman splitting of 10% result points to the formation of antiferromagnetically coupled $Mn^{2+}-Mn^{2+}$ pairs in $Cd_{11}Mn_2Se_{13}$ clusters that are the major products when the average doping concentration is high.



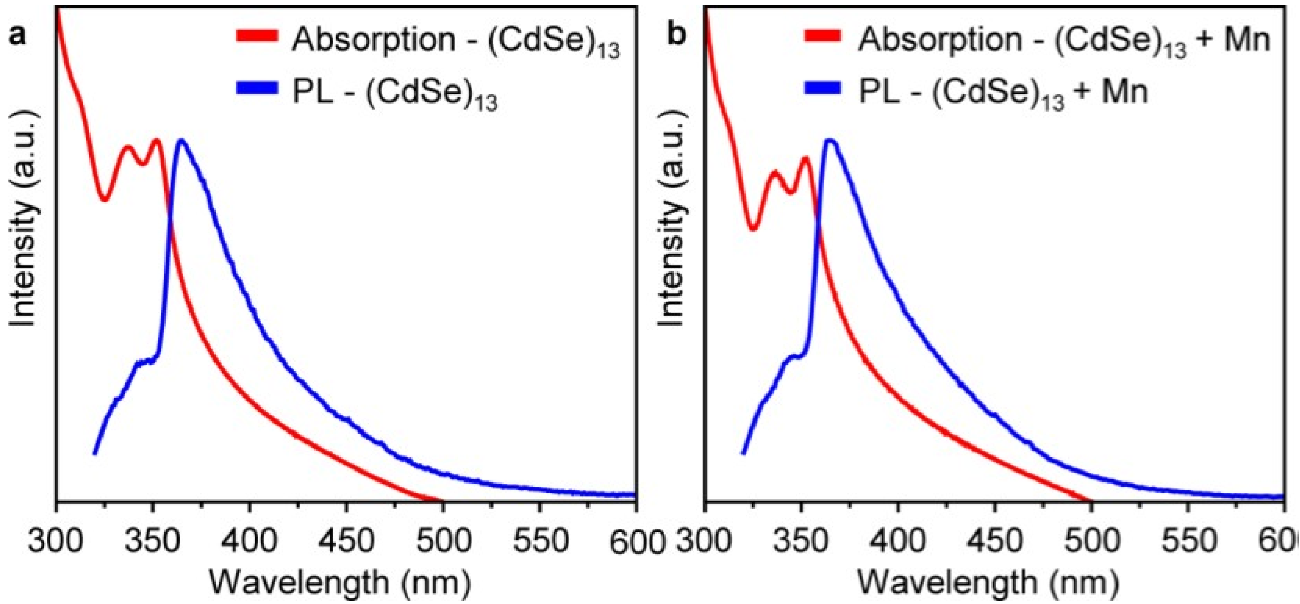
(c) Temperature-dependent MCD spectra of 4% Mn^{2+}- doped clusters under the magnetic field of 1.6 T. (d) Maximum
amplitude of the MCD signal in panel c as a function of temperature. The black curve represents a theoretical Brillouin fit.

Summary

- Successful magnetic doping of $(CdSe)_{13}$ clusters that produces the smallest dilute magnetic semiconductor is reported.

- This results uncover a previously unknown pathway for the nanoscale doping process, but they also improve the understanding of the doped semiconductors at the interface of molecules and quantum dots, which paves the way for future applications of nanoscale spin-based devices.

Thank you


a
Absorption - (CdSe)13
PL - (CdSe)13
Intensity (a.u.)
300
350
400
450
500
550
600
Wavelength (nm)
b
Absorption - (CdSe)13 + Mn
PL - (CdSe)13 + Mn
Intensity (a.u.)
300
350
400
450
500
550
Wavelength (nm)