Electronic Supplementary Information

Excitonic Zeeman Splittings in Colloidal CdSe Quantum Dots Doped with Single Magnetic Impurities

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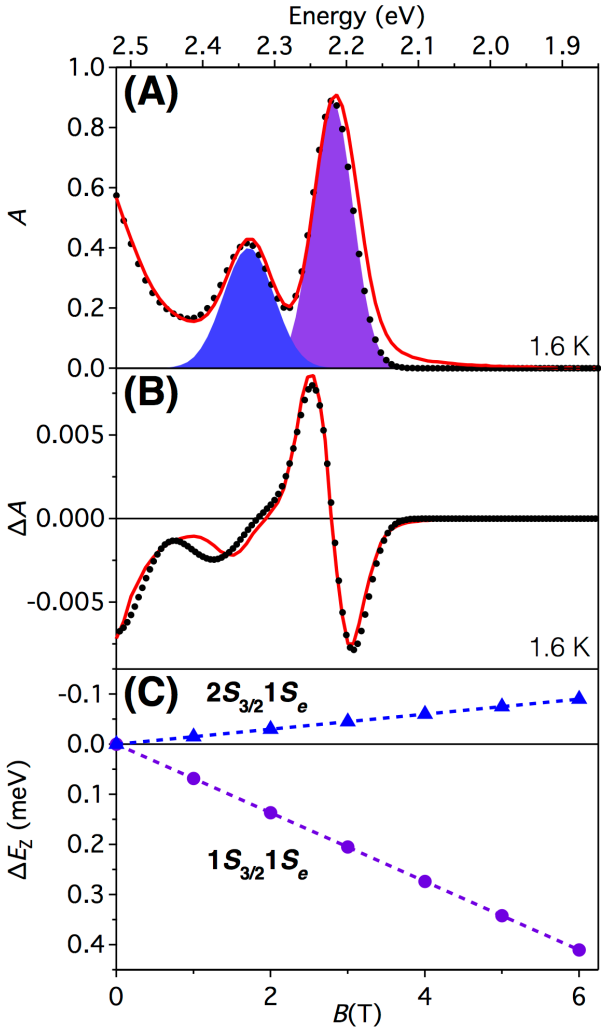

Figure S-1. (A) 1.6 K Electronic absorption and **(B)** 6 T MCD spectra (red lines) of undoped d ~4 nm CdSe QDs prepared according to the methods described in refs. 1,2. A simultaneous fit of the data to multiple Gaussian peaks (purple and blue curves shown for the first two excitonic transitions) yields the black dots. **(C)** Field-dependent Zeeman splittings of the first two excitonic transitions, displaying characteristic g values of +1.2 ($1S_{3/2}1S_e$; purple circles) and –0.3 ($2S_{3/2}1S_e$; blue triangles). MCD spectra at lower fields are omitted for clarity.

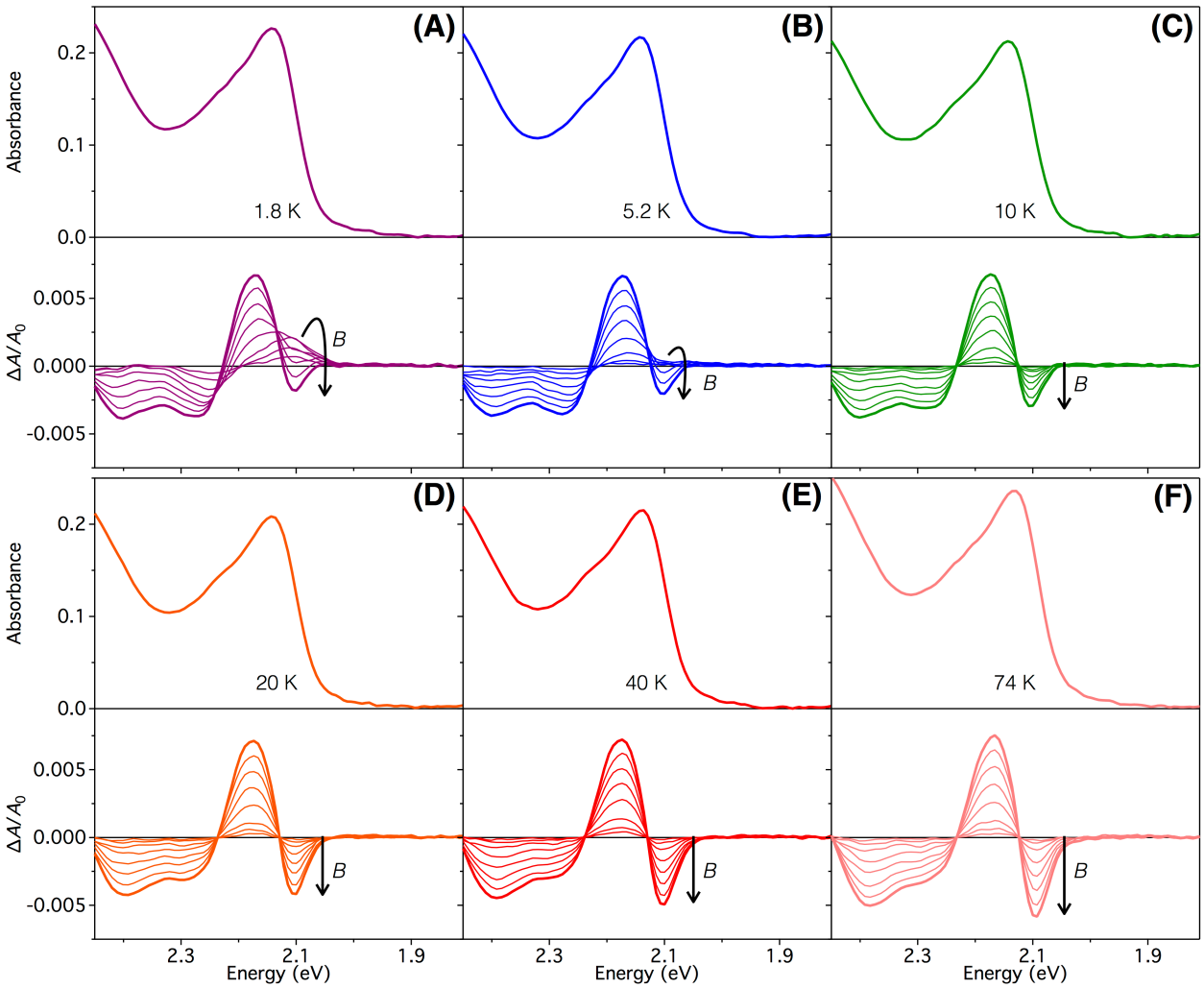

Figure S-2. Electronic absorption (top) and 0–6 T MCD (bottom) spectra of diffusion-doped d = 5.1 nm $Cd_{0.9997}Mn_{0.0003}Se$ QDs collected at 1.8 **(A)**, 5.2 **(B)**, 10 **(C)**, 20 **(D)**, 40 **(E)**, and 74 K **(F)**. The arrows indicate the direction of increasing magnetic field.

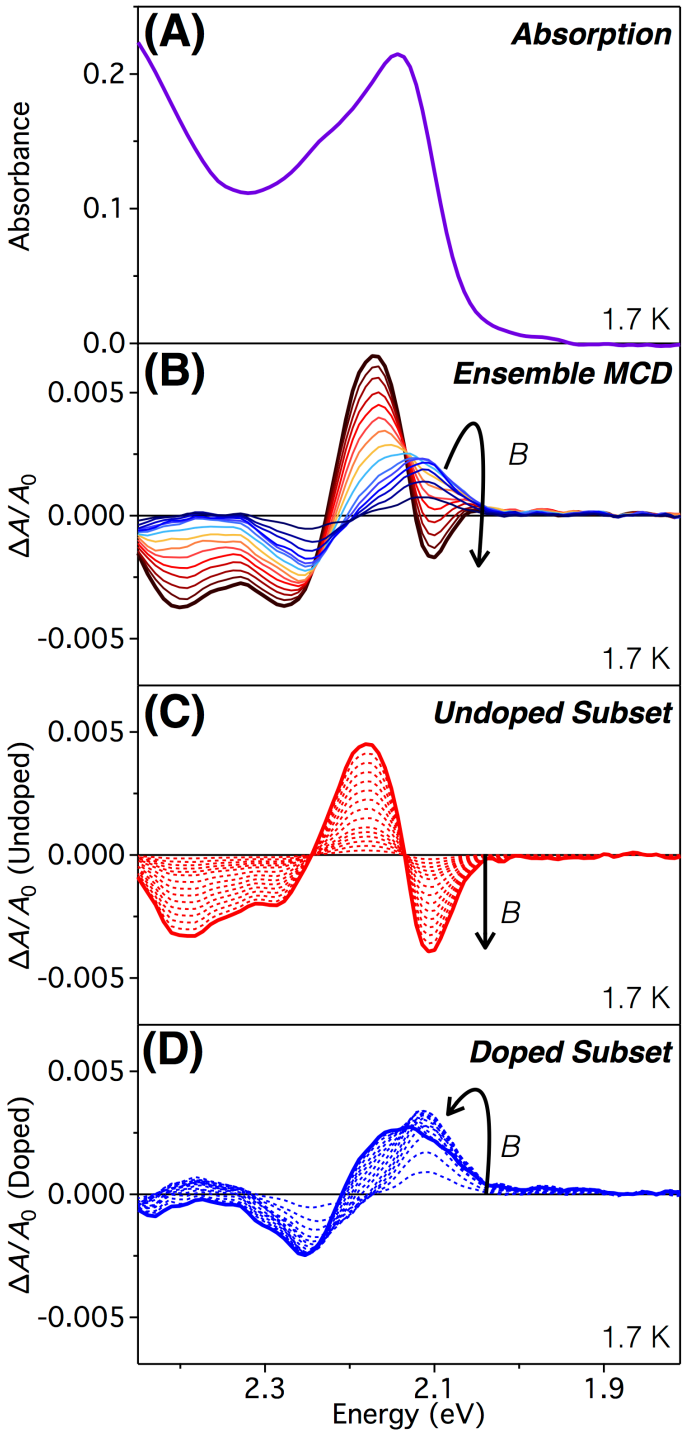

Figure S-3. (A) 1.7 K electronic absorption spectrum (purple) of diffusion-doped d = 5.1 nm $Cd_{0.9997}Mn_{0.0003}Se$ QDs **(B)** Variable-field (0–6 T; blue to red lines) MCD spectra of the same QDs at 1.7 K. **(C)** Deconvolved MCD spectra (red) of the undoped subset of this ensemble (67.8%), consisting of a purely intrinsic component to the excitonic Zeeman splittings. **(D)** Deconvolved MCD spectra (blue) of the doped subset of this ensemble (32.2%) consisting of both intrinsic and *sp–d* exchange contributions to the excitonic Zeeman splittings. The arrows indicate the direction of increasing magnetic field.

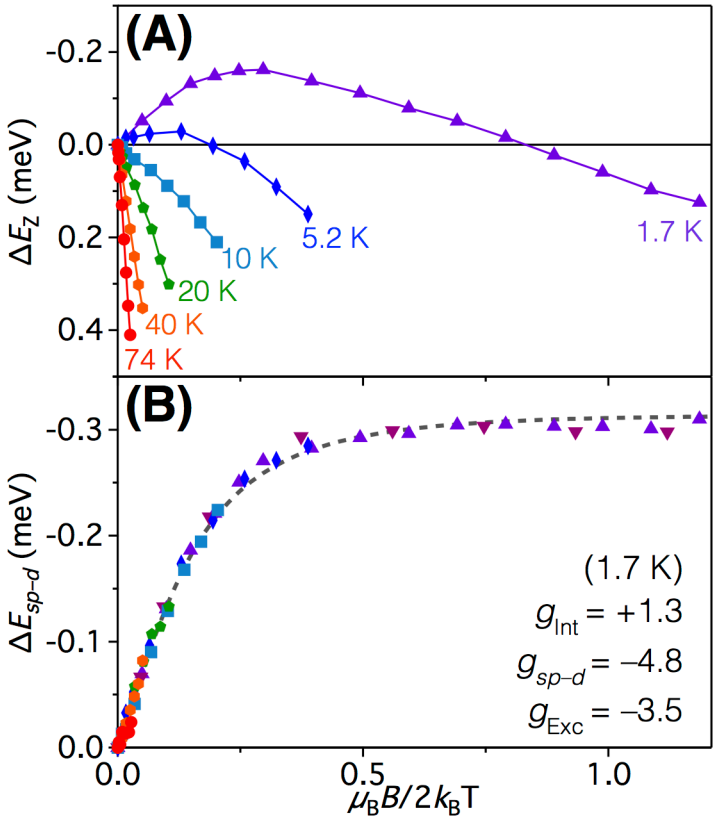

Figure S-4. (A) Excitonic Zeeman splittings of the $1S_{3/2}1S_e$ transition in diffusion-doped d = 5.1 nm $Cd_{0.9997}Mn_{0.0003}Se$ QDs, determined from analysis of VT-V*B* MCD spectra (Figure 2B in the Main Text) **(B)** Brillouin saturation magnetization of the *sp–d* exchange contribution to the $1S_{3/2}1S_e$ Zeeman splittings as determined from VT-V*B* MCD spectra. The values of g_{Int} = +1.3 and g_{sp-d} = –4.8 are calculated from the low-field (Curie) limit at 1.7 K for the $1S_{3/2}1S_e$ transition. Data in purple upward triangles, maroon downward triangles, dark blue diamonds, light blue squares, green pentagons, orange hexagons, and red circles correspond to analysis of 0–6 T MCD spectra collected at 1.7, 1.8, 5.2, 10, 20, 40, and 74 K, respectively. The gray dashed line represents a fit of these data to Equation 3 of the main text.

Table S1. G values obtained from fitting the ΔE_Z data of Figures 2–3 ($Cd_{0.9997}Mn_{0.0003}Se$ QDs) and S-1 (undoped CdSe QDs) in the low-field (Curie) limit.

	$1S_{3/2}1S_e$		$2S_{3/2}1S_e$	
	CdSe	$Cd_{0.9997}Mn_{0.0003}Se$	CdSe	$Cd_{0.9997}Mn_{0.0003}Se$
g_{Int}	+1.2	+1.3	–0.3	–0.2
g_{sp-d}	0	–4.8	0	–3.6

References

(1) Vlaskin, V. A.; Barrows, C. J.; Erickson, C. S.; Gamelin, D. R., Nanocrystal Diffusion Doping. *J. Am. Chem. Soc.* **2013,** *135*, 14380−14389.

(2) Barrows, C. J.; Chakraborty, P.; Kornowske, L. M.; Gamelin, D. R., Tuning Equilibrium Compositions in Colloidal $Cd_{1-x}Mn_xSe$ Nanocrystals Using Diffusion Doping and Cation Exchange. *ACS Nano* **2016,** *10*, 910–918.