Supporting Information for:

Surface Contributions to Mn^{2+} Spin Dynamics in Colloidal Doped Quantum Dots

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Fitting analysis to obtain T_1 and T_2

Figure S1 shows inversion recovery data for $Zn_{0.995}Mn_{0.005}O$ QDs in toluene (tol, a) or deuterated toluene (tol-d_8, b), and for $Zn_{0.900}Mn_{0.010}O$ QDs washed with ethanol (EtOH, c) or deuterated ethanol (EtOD, d). The data were fit to both single (equation S1a, dashed blue) and double (equation S1b, dotted orange) exponentials[1] to obtain T_1. From the double exponential fits, an effective spin-lattice relaxation time was calculated (T_{1eff}) using equation S1c. The results of this analysis are presented in Table S1. The T_{1eff} values determined from this analysis are reported in the main text as T_1 values.

$$V(\tau) = 1 - V_0 \exp(-\tau / T_1) \quad \text{(S1a)}$$

$$V(\tau) = 1 - A\exp(-\tau / T_{1A}) - B\exp(-\tau / T_{1B}) \quad \text{(S1b)}$$

$$T_{1eff} = \frac{A}{A+B}T_{1A} + \frac{B}{A+B}T_{1B} \quad \text{(S1c)}$$

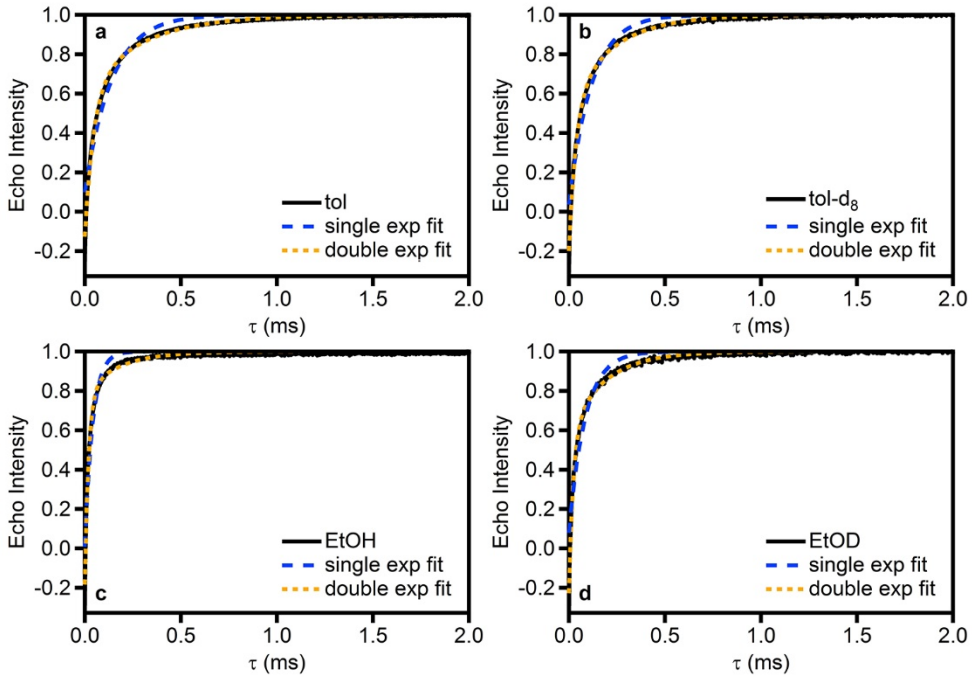

Figure S1. Inversion recovery data (solid black) with single (dashed blue) and double (dotted orange) exponential fits following equations S1a and S1b, respectively. Data are shown for $Zn_{0.995}Mn_{0.005}O$ QDs in tol (a) or tol-d_8 (b) and for $Zn_{0.900}Mn_{0.010}O$ QDs washed with EtOH (c) or EtOD (d).

Table S1. Spin-lattice relaxation times in $Zn_{0.995}Mn_{0.005}O$ (tol vs tol-d_8) and $Zn_{0.990}Mn_{0.010}O$ (EtOH vs EtOD) QDs.

	Single Exponential Fits	Double Exponential Fits				
	T_1 (μs)	T_{1A} (μs)	A	T_{1B} (μs)	B	T_{1eff} (μs)
In tol	139 ± 2	298 ± 3	0.342 ± 0.004	46.6 ± 0.6	0.658 ± 0.005	151 ± 2
In tol-d_8	117 ± 1	230 ± 2	0.374 ± 0.005	37.4 ± 0.5	0.625 ± 0.005	109 ± 1
With EtOH	41 ± 1	179 ± 5	0.177 ± 0.005	19.7 ± 0.3	0.823 ± 0.007	48 ± 1
With EtOD	84 ± 1	184 ± 2	0.338 ± 0.004	22.4 ± 0.4	0.662 ± 0.006	80 ± 1

Figure S2 shows 2-pulse ESEEM data for $Zn_{0.995}Mn_{0.005}O$ QDs in toluene (tol, a) or deuterated toluene (tol-d_8, b), and for $Zn_{0.900}Mn_{0.010}O$ QDs washed with ethanol (EtOH, c) or deuterated ethanol (EtOD, d). The data were fit to both single (equation S2a, dashed blue) and double (equation S2b, dotted orange) exponentials[1] to obtain T_2. From the double exponential fits, effective spin-lattice relaxation times were calculated (T_{2eff}) using equation S2c. The results of this analysis are presented in Table S2. For EtOD, a double exponential fit does not converge when $T_{1A} \neq T_{1B}$, so a single exponential fit was used. In the main text, T_{2eff} from this analysis is

reported for comparison between tol and tol-d_8, and T_2 from this analysis is reported for comparison between EtOH and EtOD.

$$V(\tau) = V_0 \exp(-2\tau / T_2) \tag{S2a}$$

$$V(\tau) = A\exp(-2\tau / T_{2A}) + B\exp(-2\tau / T_{2B}) \tag{S2b}$$

$$T_{2\text{eff}} = \frac{A}{A+B}T_{2A} + \frac{B}{A+B}T_{2B} \tag{S2c}$$

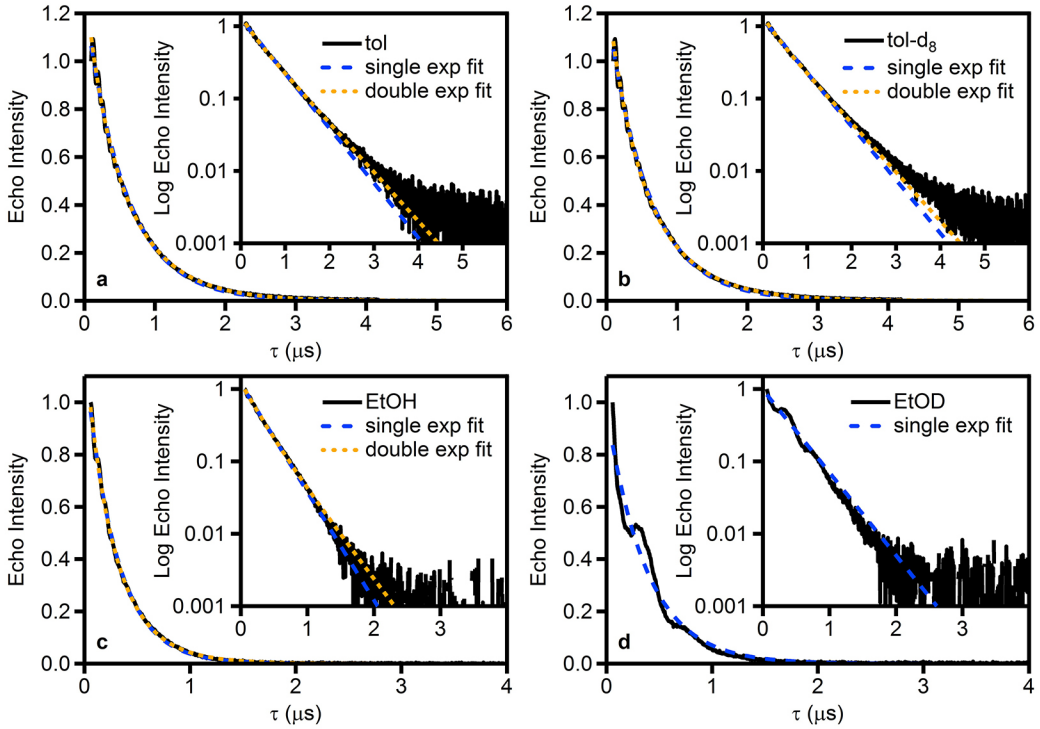

Figure S2. Hahn echo decay data (solid black) with single (dashed blue) and double (dotted orange) exponential fits following equations S2a and S2b, respectively. Decays are shown for $Zn_{0.995}Mn_{0.005}O$ QDs in tol (a) or tol-d_8 (b) and for $Zn_{0.900}Mn_{0.010}O$ QDs washed with EtOH (c) or EtOD (d).

Table S2. Spin-lattice relaxation times in $Zn_{0.995}Mn_{0.005}O$ (tol vs tol-d_8) and $Zn_{0.990}Mn_{0.010}O$ (EtOH vs EtOD) QDs.

	Single Exponential Fits	Double Exponential Fits				
	T_2 (μs)	T_{2A} (μs)	A	T_{2B} (μs)	B	$T_{2\text{eff}}$ (μs)
In tol	1.150 ± 0.002	1.28 ± 0.01	0.77 ± 0.01	0.49 ± 0.02	0.23 ± 0.01	1.10 ± 0.02
In tol-d_8	1.176 ± 0.002	1.36 ± 0.01	0.70 ± 0.02	0.60 ± 0.03	0.30 ± 0.02	1.13 ± 0.03
With EtOH	0.581 ± 0.001	0.73 ± 0.03	0.47 ± 0.02	0.43 ± 0.02	0.53 ± 0.02	0.57 ± 0.03
With EtOD	0.76 ± 0.01					

Figure S3 shows inversion recovery (a) and 2-pulse ESEEM data (b) collected on $Cd_{0.996}Mn_{0.004}Se$ QDs before (blue) and after (red) CdSe shell growth. To obtain T_1 and T_2 the inversion recovery and 2-pulse ESEEM spectra were fit to equations S1a and S2a, respectively.

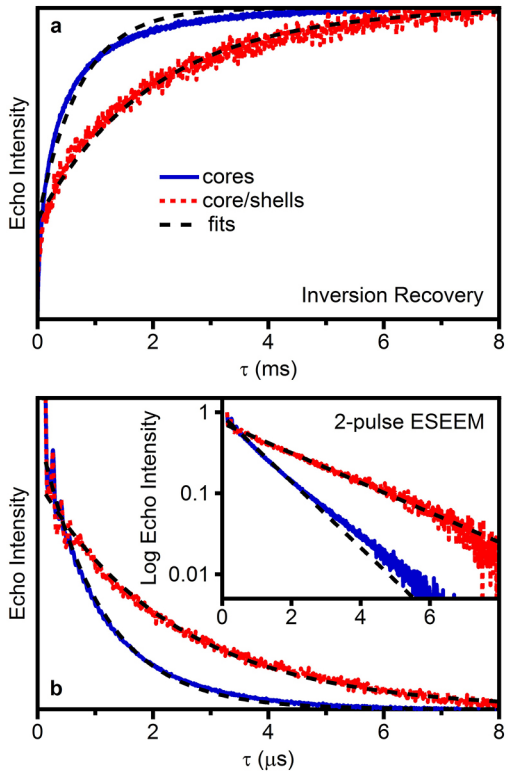

Figure S3. pEPR data collected on $Cd_{0.996}Mn_{0.004}Se$ QDs before (blue) and after (red) CdSe shell growth. (a) Echo-detected inversion recovery (T_1) and (b) 2-pulse spin-echo decay (T_2). The dashed black lines are single exponential fits to the inversion recovery and 2-pulse ESEEM data following equations S1a and S2a, respectively.

Estimated dipole-dipole contributions assuming non-uniformly doped core QDs or dopant migration during shell growth

If an undoped core nucleus volume with d = 2.0 nm is assumed,[2] then the average Mn^{2+} position is ~0.2 nm from the nearest QD surface. Upon shell growth this distance increases to ~1.3 nm. The $1/r^6$ dependence of dipole-dipole coupling leads to $T_{dip}^{core/shell} / T_{dip}^{core} \approx 3\times10^4$. Table S3 summarizes the results in this scenario. Similar results are obtained even if the Mn^{2+} position is randomized throughout the core/shell volume, for example by diffusion during shell growth,[3] although this scenario is not considered likely.

Table S3. Intrinsic and dipolar contributions to spin relaxation times in core and core/shell nanocrystals under the assumption of an undoped core nucleus with d = 2.0 nm, determined using equation 1 of the main text.

	T_0	T_{dip}^{core}	$T_{dip}^{core/shell}$
Spin-lattice (T_1)	2.01 ms	1.13 ms	34.0 s
Spin-spin (T_2)	4.70 μs	3.90 μs	117 ms

References

(1) Schweiger, A.; Jeschke, G. *Principles of Pulse Electron Paramagnetic Resonance*; Oxford University Press: United Kingdom, 2001.

(2) Norberg, N. S.; Parks, G. L.; Salley, G. M.; Gamelin, D. R. Giant Excitonic Zeeman Splittings in Colloidal Co^{2+}-Doped ZnSe Quantum Dots. *J. Am. Chem. Soc.* **2006**, *128*, 13195-13203.

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