

Supporting Information

# Thermodynamics of Dual Doping in Quantum Dots

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**Experimental Section:**

**Chemicals used.** Cobalt acetylacetonate ( $\text{Co}(\text{acac})_2$ ), iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ), platinum acetylacetonate ( $\text{Pt}(\text{acac})_2$ ), 1,2-hexadecanediol, cadmium oxide ( $\text{CdO}$ ), oleic acid (OA, 90 %), 1-octadecene (ODE, 90 %), oleylamine (OIAm, technical grade 70 %), and sulfur powder (S, 99.5 %) were purchased from Sigma Aldrich. Ethanol,

acetone, and hexane were purchased from Merck (emparta). All purchased chemicals and solvents were used without further purification.

**Synthesis of CoPt QDs.** CoPt QDs were first synthesized via co-reduction of metal salts cobalt acetylacetonate (0.05 mmol) and platinum acetylacetonate (0.05 mmol).

These metal salts were dissolved in 4 mL oleylamine and 1 mL oleic acid in a three-necked flask. The system was degassed at 80 °C for two hours under constant stirring.

The temperature was raised to 200 °C after degassing and kept under constant argon flow. After 10 minutes, the temperature of the reaction mixture was raised to 300 °C gradually (10 °C/3 min). After attaining the temperature, the reaction mixture was kept at 300 °C for 20 minutes and then cooled down to room temperature. The black precipitate was isolated by centrifuging and was then washed twice with hexane, ethanol and a few drops of acetone.

**Synthesis of FePt QDs.** The FePt core was synthesized by thermal decomposition of  $\text{Fe}(\text{CO})_5$ , and reduction of  $\text{Pt}(\text{acac})_2$  using 1,2-hexadecanediol at high temperature.

Oleic acid and oleylamine were used as coordinating agents and solvents. For the synthesis, 0.1 mmol of  $\text{Pt}(\text{acac})_2$ , 0.3 mmol of 1,2-hexadecanediol were taken in a

three-necked round bottom flask. After fitting with the condenser, 2 mL of oleic acid and 6 mL of oleylamine were added to it followed by the addition of 0.3 mmol of iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) under vacuum. The system was degassed at 80 °C for two hours under constant stirring. The temperature was raised to 200 °C after degassing and kept under constant argon flow. After 10 minutes the temperature of the reaction mixture was raised to 300 °C gradually (10 °C/3 min). After attaining the temperature, the reaction mixture was kept at 300 °C for 10 minutes and then cooled down to room temperature. Then, the as-synthesized QDs were isolated by centrifugation, washed one time by the addition of ethanol-hexane mixture and a few drops of acetone, and used for the further synthesis of clustered and diffused QDs.

**Synthesis of Core-shell MPt/CdS (M=Co, Fe) QDs.** For the synthesis of clustered MPt/CdS QDs, SILAR technique was followed where 0.2 M cadmium oleate ( $\text{Cd}(\text{Ol})_2$ ) solution was prepared using modified literature methods and 0.2 M solution of S/ODE solution was prepared by dissolving S powder in ODE in an inert atmosphere. Approximately 20 mg of presynthesized MPt (M=Co, Fe) QDs dissolved in 3 mL oleylamine, were taken in a three-necked round bottom flask and 6 mL of ODE was

added to it. The system was degassed at 80 °C for 2 hours under constant stirring. After degassing, the reaction temperature was raised to 250 °C under argon flow (for FePt QDs) and 220 °C for CoPt QDs. Overcoating was started with the addition of a stoichiometric amount of S-precursor i.e. S-ODE and was kept for 10 minutes. After 10 minutes the same amount of Cd precursor was injected into the system and annealed for 20 minutes. The cyclic addition of S precursor followed by Cd precursor was continued until an ultra-thick shell of CdS was formed over the core MPt QDs. The reaction was stopped at the required thickness of the CdS shell. The samples were washed by centrifugation using hexane-ethanol mixture and a few drops of acetone.

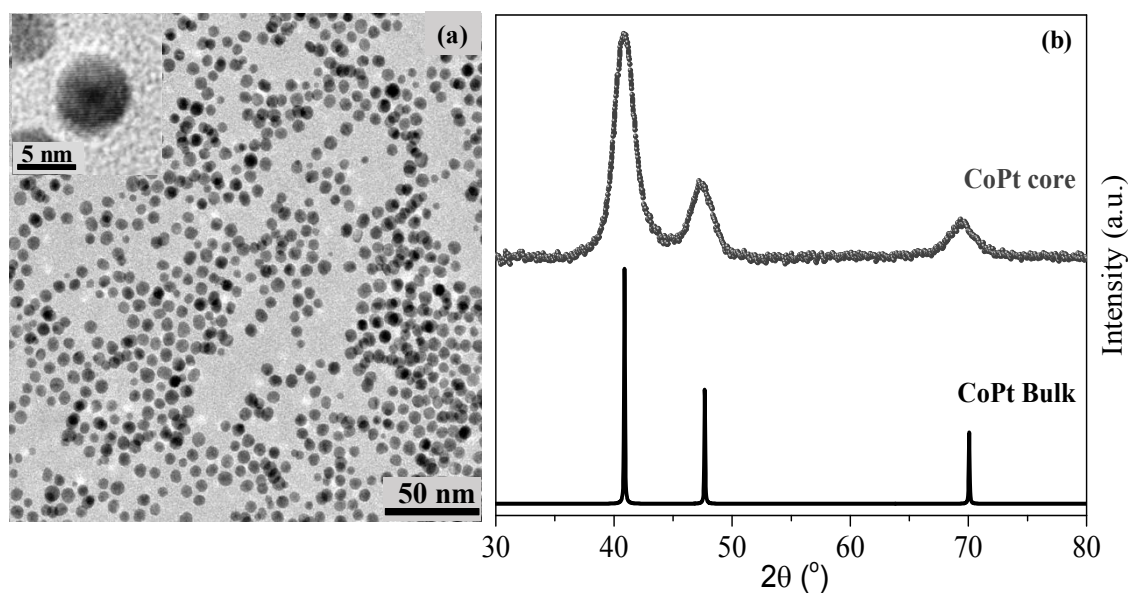
**Synthesis of Diffused MPt/CdS (M=Co, Fe) QDs.** For the synthesis of the diffused QDs, the same procedure was followed as in the case of clustered QDs. Here, for the growth of each shell, the system was annealed at 220 °C (for CoPt) and at 250 °C (for FePt) for three hours. Thick shell formation develops a strain and annealing at high temperature allows the core to diffuse inside the CdS matrix. Again, few layers of CdS

were grown and annealing procedure was continued in order to get a completely diffused QDs.

**Structural & Magnetic Characterization.** The as-synthesized QDs were characterized and studied through different techniques. QD size and shape identification were carried out using transmission electron microscopy (TEM). TEM and high-angle annular dark-field imaging (HAADF) and Energy-dispersive X-ray spectroscopy (EDS) mapping was performed on a Technai F30 UHR version electron microscope; using a field emission gun (FEG) operating at an accelerating voltage of 200 kV in bright field mode using Cu coated holey carbon TEM grids. HRTEM were performed on FEI TITAN<sup>3</sup>™ 80–300 kV aberration corrected transmission electron microscope. Crystal structure identification of the particles was carried out using X-ray diffraction, recorded on Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation. Perkin Elmer inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to obtain the elemental percentages present in the QDs. DC magnetization measurements were carried out in a superconducting quantum interference device that employs the technique of vibrating sample magnetometer (SQUID-VSM) (Magnetic Property

Measurement System MPMS-3, Quantum Design, U.S.). Few milligrams of the sample was packed in a piece of Teflon for the measurement. M vs H measurements were carried out at 2 K. FC and ZFC measurements were performed for the temperature range of 2 K to 390 K using 200 Oe constant magnetic field. The sample was first cooled from 400 K (above the ordering temperature of the sample) to 2 K in the absence of an external magnetic field. With heating, magnetization data was recorded in the field strength of 200 Oe (ZFC measurement). In the FC measurement, the sample was cooled in the presence of a magnetic field of 200 Oe. The magnetization was then recorded with temperature up to 390 K in the presence of an applied field. X-ray absorption fine structure (XAFS) spectroscopy was employed to probe the local structure around Co and Pt for core, clustered and diffused QDs. The measurement was carried out at the Stanford Synchrotron Radiation Light source, SLAC National Accelerator Laboratory. Data collected was processed using Athena and Artemis software.<sup>1</sup> The absorption spectrum of the sample was recorded using an Agilent 8453 UV visible spectrometer. Steady-state PL spectrum was obtained using a 450 W xenon lamp as the source. Combining TEM, XRD, XAFS and SQUID measurements,

we characterized and studied the magnetic response of core, clustered and diffused QDs.



**Figure S1.** (a) TEM image showing CoPt core [6.6 ± 0.56 nm] QDs and the representative high-resolution TEM in the inset (b) XRD pattern of CoPt core QDs.

**Table S1.** ICP-OES data for CoPt core, CoPt/CdS core-shell and Co,Pt diffused CdS QDs.

System	Co %	Pt %	Cd %
CoPt core (6.6 nm)	68.8	31.2	-
CoPt core (10 nm)	70.0	30.0	-
CoPt/CdS core-shell system (11.3 nm)	16.3	21.5	62.2
CoPt/CdS diffused system (10.9 nm)	2.3	3.5	94.2

CoPt/CdS diffused system (17.3 nm)	0.75	1.46	97.79
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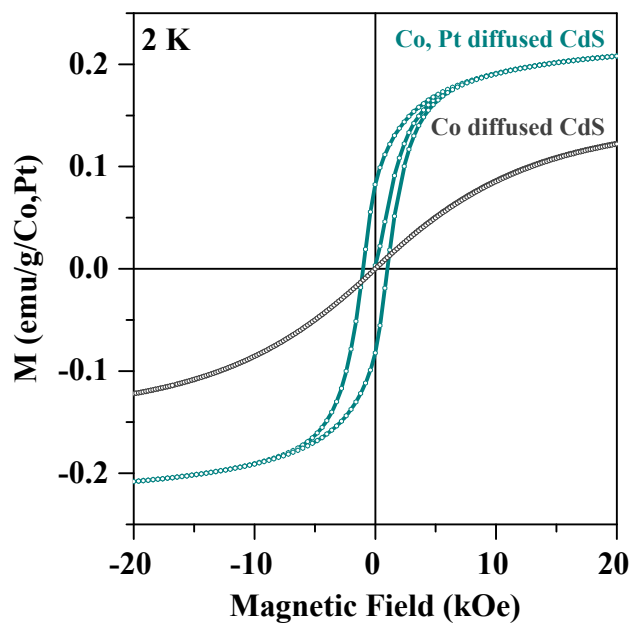
**TABLE S2.** List of fit parameters (Independent Points ( $N_{idp}$ ) and Number of variables ( $N_{var}$ ) for the fit, Bond length (R), coordination number (N), Debye-Waller factor ( $\sigma^2$ ), energy shift ( $\Delta E$ ) and R-factor) obtained from modeling the data for Co-K edge and Pt-L<sub>3</sub> edge.

Sample	Paths	R (Å)	N	$\sigma^2$	$\Delta E$ (eV)	R-factor
Co edge Core Nidp = 14 Nvar =7	Co_Pt	2.69 ±	0.96 ±	0.005	-2.57±	0.01
	Co_Co	0.01	0.01	0.01	3.12	
	Co_O	4.06 ±	0.52 ±	0.016		
		0.23	0.08			
		1.99 ±	2.49 ±			
		0.13	0.02			
Co edge CoPt/CdS core-shell Nidp = 14 Nvar =8	Co_Pt	2.71 ±	3.52 ±	0.009	3	0.08
	Co_Co	0.001	0.07	0.007		
	Co_S	3.74 ±	0.37 ±	0.004		
	Co_O	0.08	0.12	0.004		
		2.35 ±	0.63 ±			
		0.17	0.06			
		1.92 ±	0.17 ±			
	0.21	0.03				
Co edge CoPt/CdS diffused	Co_Pt	2.70 ±	1.96 ±	0.005	7.13± 3.31	0.05
	Co_Co	0.003	0.07	0.007		
	Co_S					

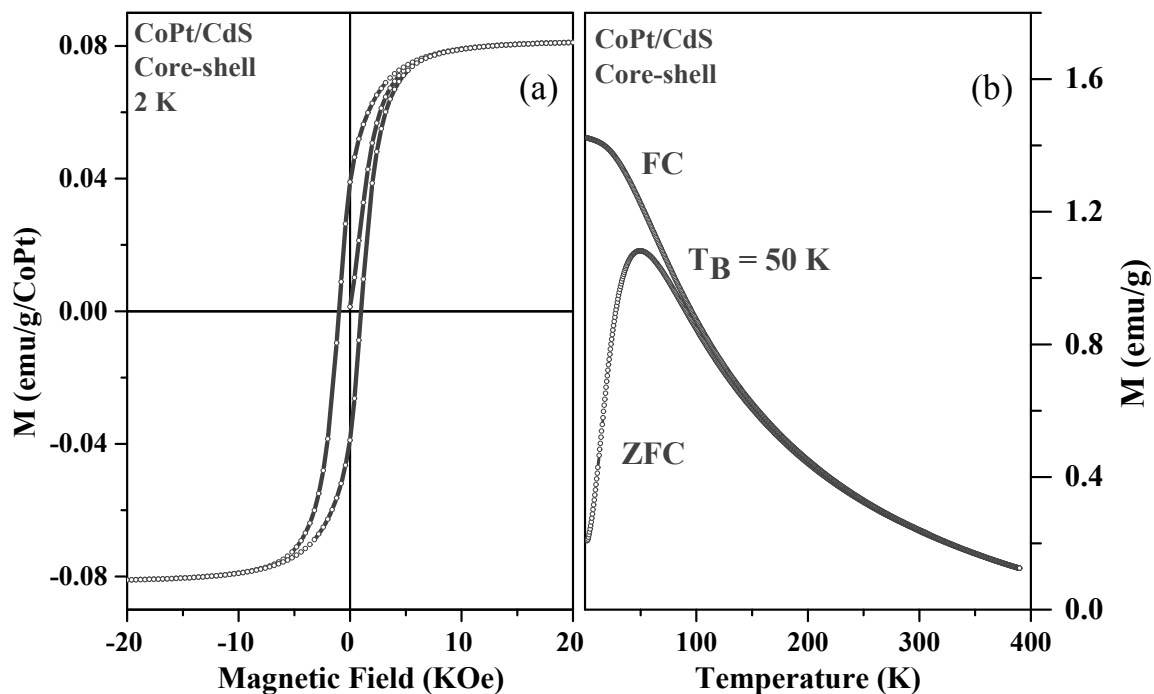


Nidp = 14 Nvar =8		3.67 ± 0.16 2.35 ± 0.17	0.63 ± 0.13 1.48 ± 0.11	0.004± 0.003		
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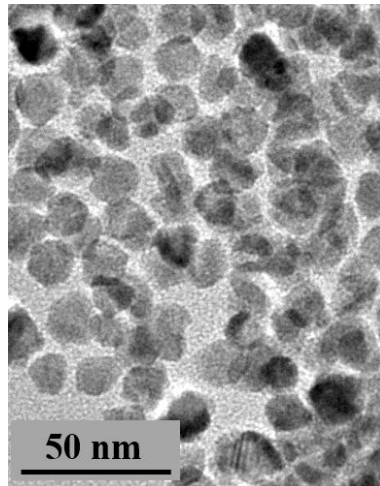
Sample	Paths	R (Å)	N	( $\sigma^2$ )	$\Delta E$ (eV)	R-factor
Pt edge Core Nidp = 14 Nvar =8	Pt_Co	2.66 ±	0.76 ±	0.006	6.91±	0.008
	Pt_Pt	0.04	0.04	0.007 ±	0.80	
	Pt_O	2.73 ±	3.77 ±	0.001		
		0.02	0.05	0.007		
		1.96 ±	0.30 ±			
		0.008	0.01			
Pt edge CoPt/CdS core-shell Nidp = 14 Nvar =7	Pt_Co	2.65 ±	1.45 ±	0.009	6.67 ±	0.008
	Pt_Pt	0.06	0.06	0.006	1.40	
	Pt_S	2.72 ±	3.56 ±	0.013		
		0.009	0.04			
		2.38 ±	0.18 ±			
		0.14	0.05			
Pt edge CoPt/CdS diffused Nidp = 14 Nvar =7	Pt_Co	2.62 ±	0.83 ±	0.009	-0.99 ±	0.02
	Pt_Pt	0.08	0.12	0.006	2.91	
	Pt_S	2.68 ±	6.83 ±	0.013		
		0.02	0.10			
		2.59 ±	1.00 ±			
		0.06	0.24			



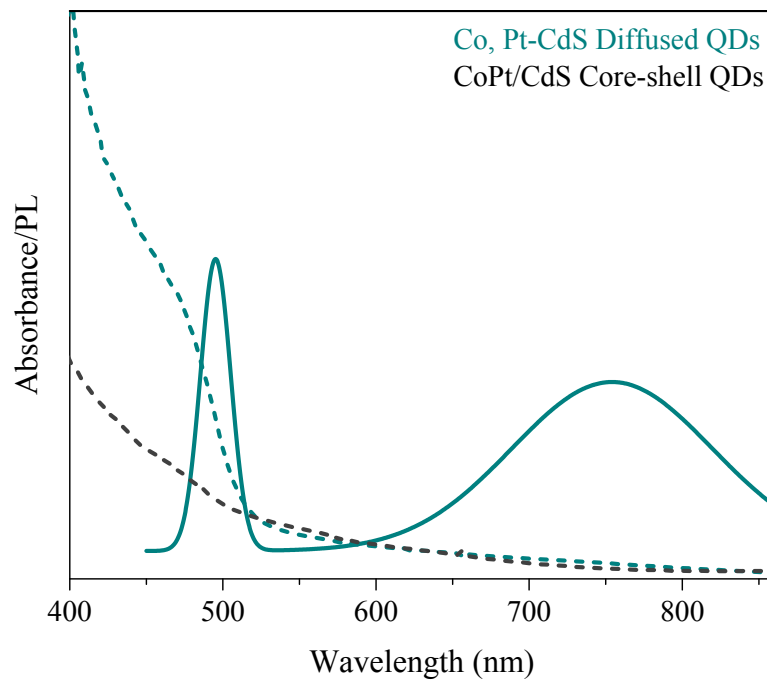
**Figure S2.** A comparison of magnetization vs. field plot for  $\sim 10$  nm Co, Pt diffused CdS QDs and Co diffused CdS QDs at 2 K.



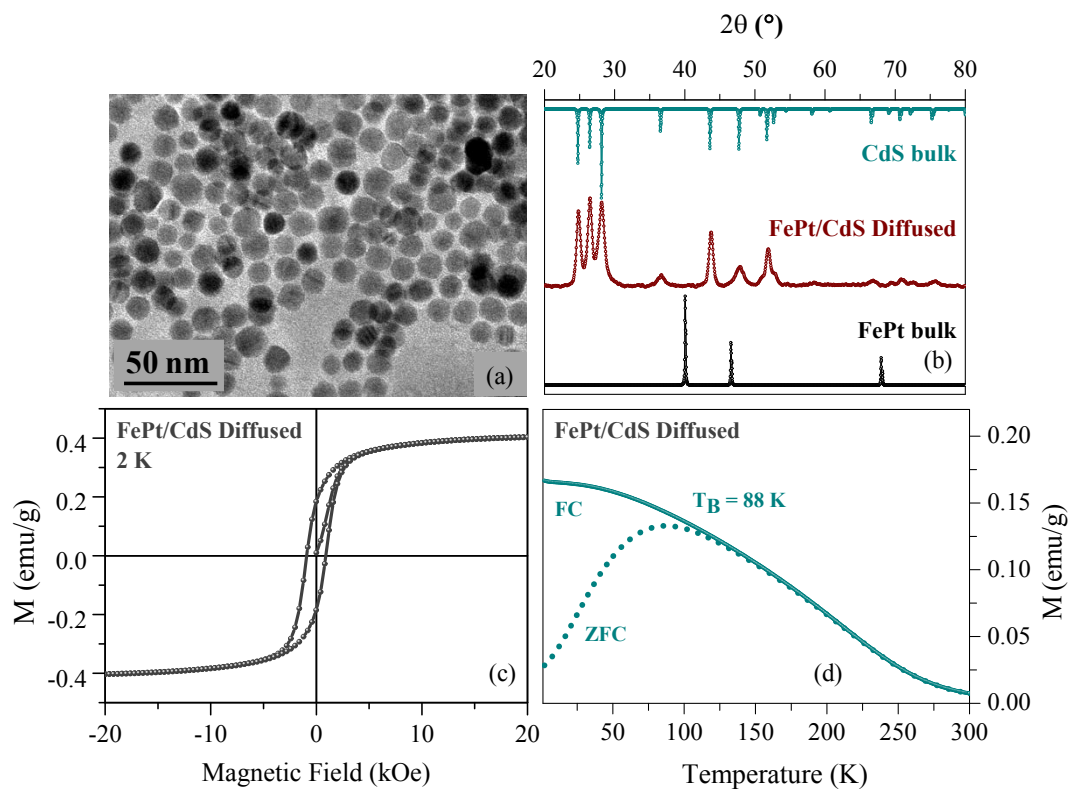
**Figure S3.** (a) Magnetization vs. magnetic field plot for CoPt/CdS core-shell QDs at 2 K. (b) FC and ZFC plots for CoPt/CdS core-shell QDs measured using 200 Oe field.



**Figure S4.** TEM image of Co, Pt-CdS diffused QDs (17.3 nm).



**Figure S5.** Steady-state PL (solid line) and absorption (dashed line) of Co, Pt-diffused CdS and CoPt/CdS core-shell QDs.



**Figure S6.** (a) TEM image of Fe, Pt-diffused CdS (b) XRD pattern of Fe, Pt diffused CdS QDs (c) Magnetization vs. magnetic field for Fe, Pt diffused CdS QDs at 2 K. (d) FC and ZFC for Fe, Pt diffused CdS QDs measured using 200 Oe field.

Reference:

(1) Ravel, B.; Newville, M. ATHENA and ARTEMIS: Interactive Graphical Data

Analysis Using IFEFFIT. *Phys. Scr.* **2005**, *2005*, 1007.