

Supporting Information for:

# Resolving the Core and the Surface of CdSe Quantum Dots and Nanoplatelets using Dynamic Nuclear Polarization Enhanced PASS-PIETA NMR Spectroscopy

*Laura Piveteau,<sup>†,‡</sup> Ta-Chung Ong,<sup>†,⊥</sup> Brennan J. Walder,<sup>§</sup> Dmitry N. Dirin,<sup>†,‡</sup> Daniele Moscheni,<sup>#</sup> Barbara Schneider,<sup>†</sup> Janine Bär,<sup>†</sup> Loredana Protesescu,<sup>†,‡</sup> Norberto Masciocchi,<sup>#</sup> Antonietta Guagliardi,<sup>#, &</sup> Lyndon Emsley,<sup>§</sup> Christophe Copéret<sup>†, \*</sup> and Maksym V. Kovalenko,<sup>†,‡, \*</sup>*

<sup>†</sup>Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1-5, CH-8093, Switzerland

<sup>‡</sup>Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Überlandstrasse 129, CH-8600, Switzerland

<sup>§</sup>Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

<sup>#</sup>Dipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria, via Valleggio 11, I-2100 Como, Italy

<sup>&</sup>Istituto di Crystallografia and To.Sca.Lab, Consiglio Nazionale delle Ricerche, via Valleggio 11, I-22100 Como, Italy

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## Characterization of NCs

### UV/VIS Absorption Spectroscopy

UV/VIS absorption spectra were collected using a JASCO V670 spectrometer.

### Transmission Electron Microscopy and Scanning Electron Microscopy

Transmission electron microscopy (TEM) and scanning electron microscopy (STEM) studies were conducted either on a JEOL JEM-2200FS microscope operating at 200 kV, a Hitachi HT 7700 microscope operating at 120 kV, a FEI Tecnai F30 operating at 300 kV or a FEI Talos F200X microscope operating at 200 kV and equipped with Super-X EDS system (4 detector configuration).

### Elemental Analysis by Energy-Dispersive X-ray Spectroscopy

The elemental distribution of Cd, Se and S within core/crown NPLs was examined by energy-dispersive spectroscopy (EDS) employed in the STEM operation mode using about 0.7-0.8 nm probe size.

### Powder X-ray Diffraction

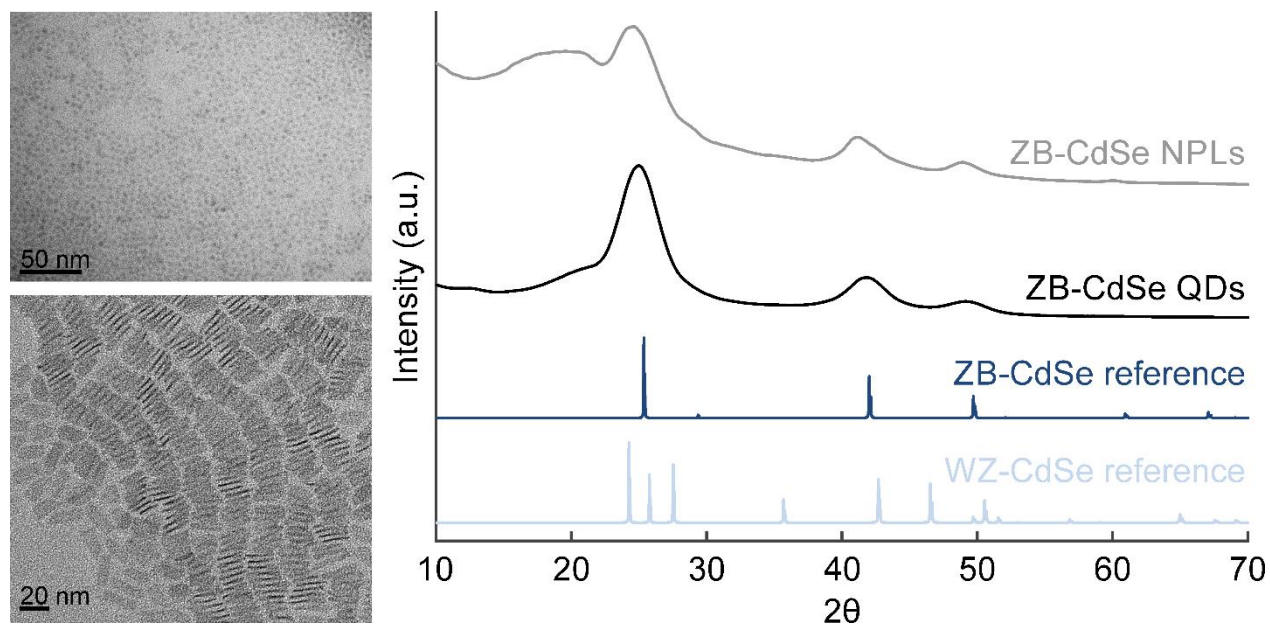
Powder X-Ray diffraction (PXRD) patterns were collected on a Stoe IPDS II single crystal diffractometer modified to acquire powder samples, equipped with an image plate detector, sealed tube with Cu-K $\alpha$ -radiation,  $\lambda = 1.54186$  Å, graphite monochromator and monicap-collimator or on a RIGAKU MINIFLEX in reflection mode with Cu-K $\alpha$ -radiation,  $\lambda = 1.54186$ .

## Synthesis of the Materials Presented in SI

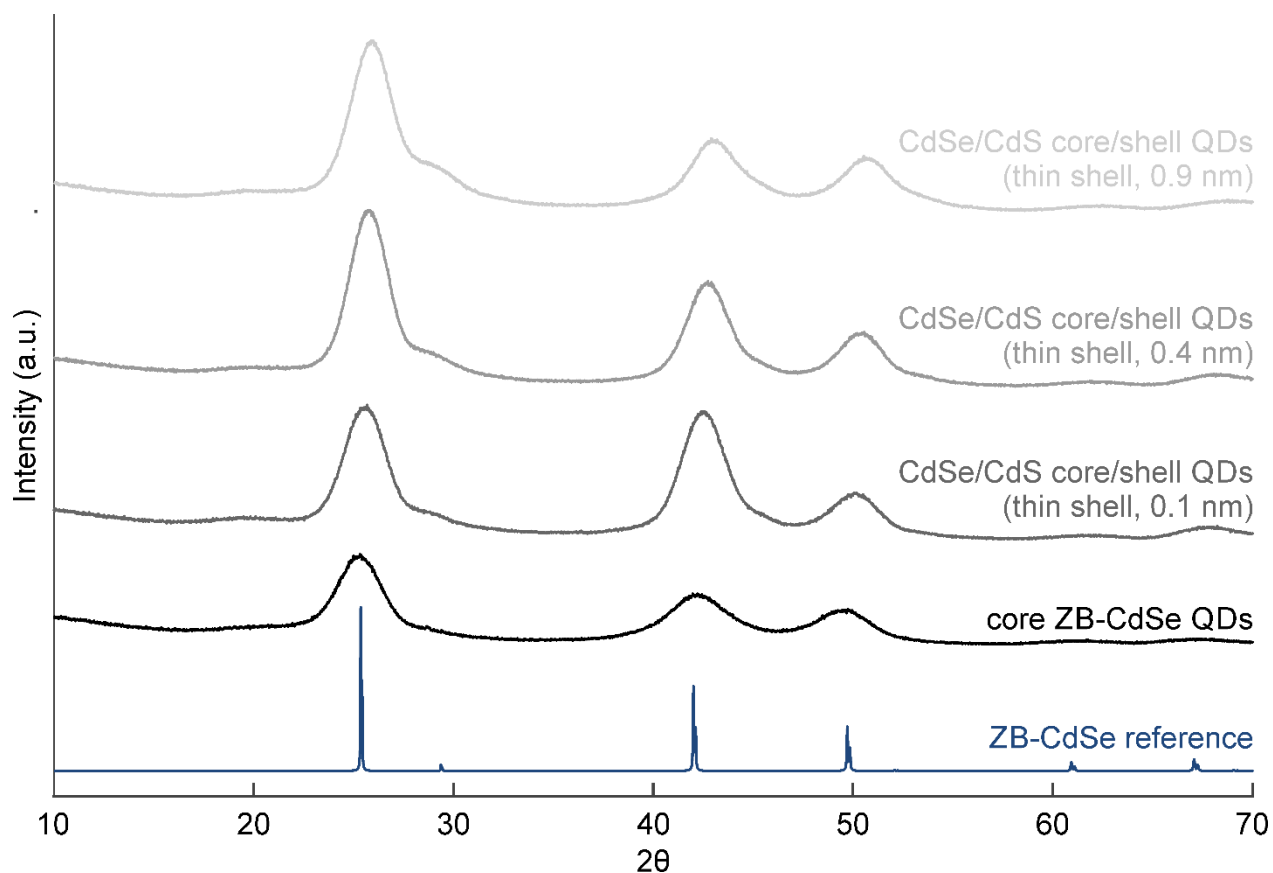
**Materials.** Cadmium acetate dihydrate ( $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , Fluka,  $\geq 98\%$ ), 2,2'-dithiobisbenzothiazole (Aldrich, 99%), myristic acid (Aldrich,  $\geq 99\%$ ), 1-octadecene (ODE, Aldrich, 90%), oleic acid (OA, Aldrich, 90%), sulfur (S, Aldrich, 99.998%), 1,1,2,2-tetrachloroethane (TCE, Aldrich), tetraethylthiuram disulfide (Aldrich,  $\geq 98\%$ ). All materials were used without further purification. The solvents butanol (BuOH), ethanol (EtOH), hexane and methanol (MeOH) were obtained from various sources.

**Oleate-capped (zinc-blende) ZB-CdS Quantum Dots (QDs)** were reproduced according to the synthesis of Cao *et al.*<sup>1</sup> with minor modifications. 46.7 mg  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.1 mmol), 95.4 mg myristic acid (0.2 mmol), 3.2 mg sulfur (0.05 mmol), 3.7 mg tetraethylthiuram disulfide and 2.1 mg 2,2'-dithiobisbenzothiazole were dissolved in 12.7 mL ODE and dried for 2 h at 120 °C under vacuum. Under Ar-flow the solution was heated to 250 °C and after 4 min cooled to room-temperature (RT). 200  $\mu\text{L}$  OA were added to the crude solution and heat was applied until a clear yellow solution was obtained as a result of the replacement of myristate with oleate at the QD surface. The QDs were washed three times by solvent/antisolvent precipitation and centrifugation, using a hexane/BuOH-MeOH-EtOH mixture (2:1:8 v/v) for the first and hexane/EtOH for second and third washings.

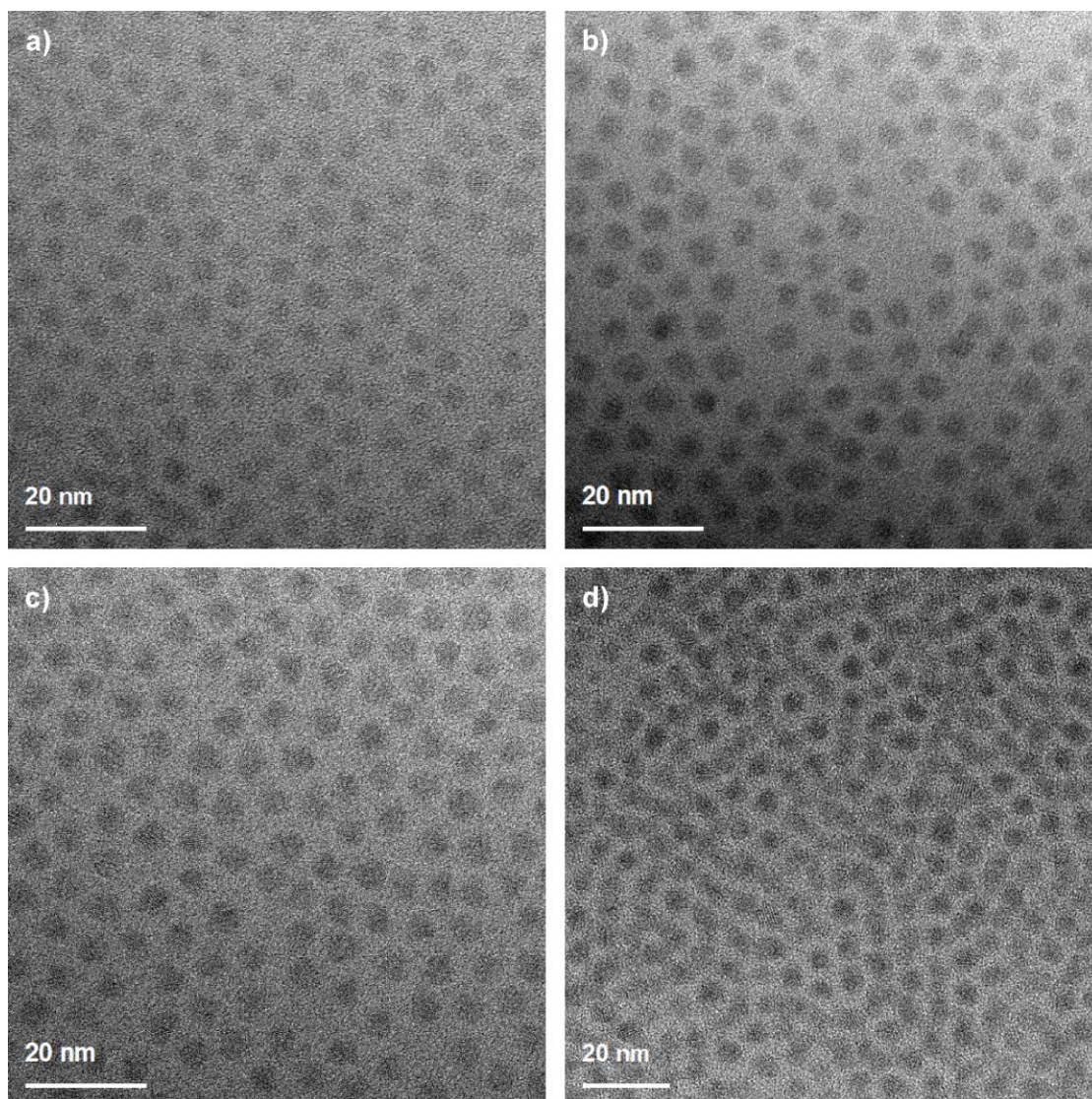
## Supplementary Figures



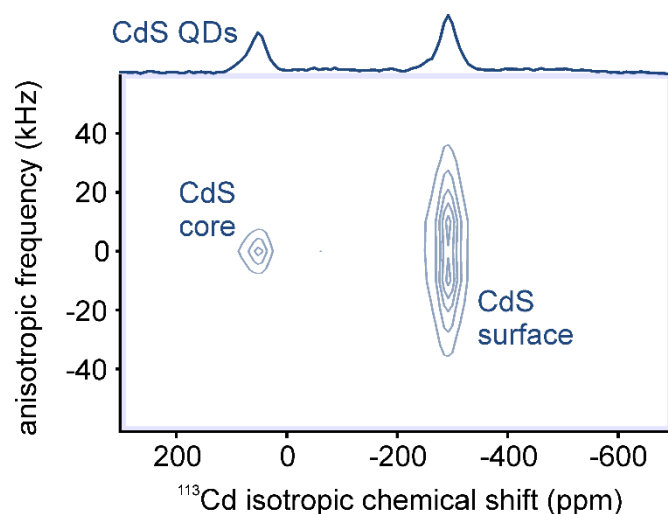
**Figure S1.** TEM images and PXRD patterns of ZB-CdSe QDs (3.0 nm diameter, top left image, black PXRD pattern) and ZB-CdSe NPLs (bottom left image, grey PXRD pattern). Comparison with wurtzite (WZ)-CdSe and ZB-CdSe references shows that both QD and NPL samples have ZB structure. The diffraction peaks are broadened due to the nanoscale dimension of the crystallites. The background signal is induced by air and polymer substrates used for the PXRD measurement.



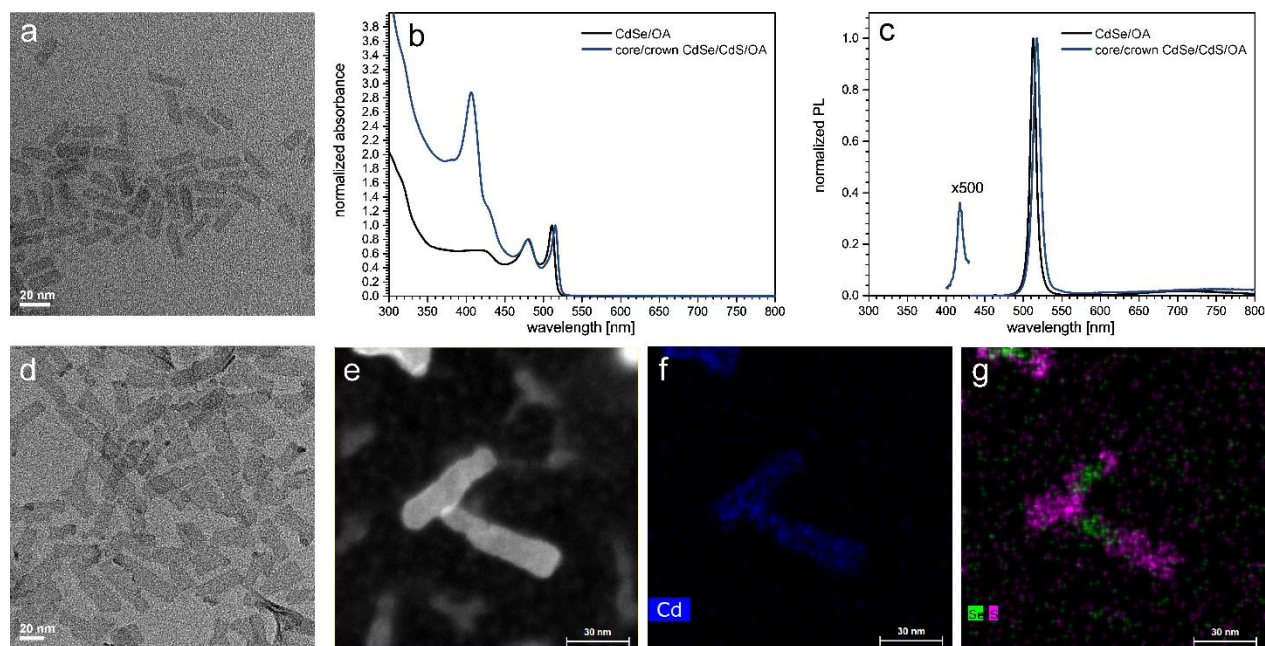
**Figure S2.** PXRD patterns of ZB-CdSe QDs of 3.6 nm size (black) before and after growth of CdS shells of 0.1, 0.4 and 0.9 nm thickness (different grey scales). By comparing with the ZB-CdSe reference pattern it can be concluded that the ZB structure of the initial NCs is maintained during shell growth. The shoulder of the (111) peak falling near 29°, is attributed to the weak (200) reflection, enhanced by the presence of sulfur, which is in agreement with the average cell shrinking.



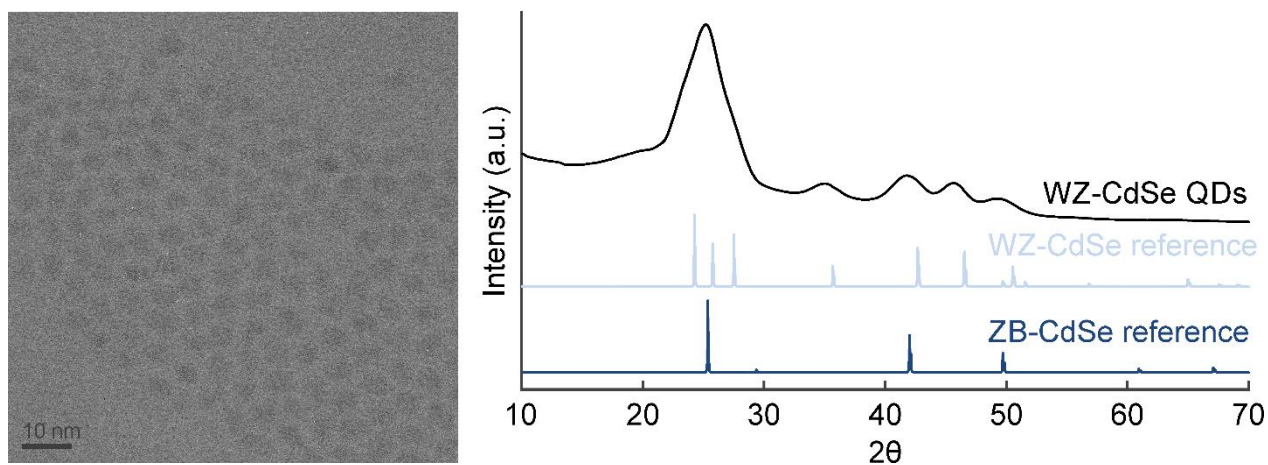
**Figure S3.** TEM images of (a) oleate-capped ZB-CdSe QDs of approximately 3.7 nm diameter (3.6 nm based on bandgap energy), onto which CdS shells of (b) 0.1 nm, (c) 0.4 nm and (d) 0.9 nm were step-wise grown by SILAR method.



**Figure S4.**  $^{113}\text{Cd}$  DNP enhanced PASS-PIETA NMR spectrum of oleate-capped ZB-CdS QDs. The signal assigned to the core CdS at 52 ppm is close to the reported value for bulk CdS (65 ppm).<sup>2</sup> The signal at -293 ppm is attributed to the surface Cd atoms.



**Figure S5.** Characterization of CdSe/CdS core/crown nanoplatelets (NPLs). Lateral crown growth is observed in TEM pictures when comparing (a) the initial CdSe NPLs with (d) the core/crown CdSe/CdS NPLs. In the absorption spectrum, the excitonic peak of CdSe remains unchanged upon shell growth as the platelet thickness stays constant. However, an additional absorption peak appears at 407 nm (b), due to the formation of CdS shell. The CdS shell is only weakly luminescent (peak at 418 nm, magnified 500-fold). Photoluminescence from CdSe shifts only slightly (c), again in agreement with the preservation of the platelet thickness. A high-angle annular dark field STEM image of two core/crown CdSe/CdS NPLs is depicted in (e). Of the same NPLs, a Cd-color map (f) and a composite of S- (pink) and Se- (green) color maps (g) were extracted from an EDS-STEM hypermap. A homogeneous Cd-distribution is visible over the whole platelet, while S and Se are located in different regions.



**Figure S6.** TEM image and PXRD of WZ-CdSe QDs (3.6 nm size, estimated according to absorption spectrum in Figure 5). Comparison with WZ-CdSe and ZB-CdSe references proves the QDs to have WZ crystal structure. The diffraction peaks are broadened due to the nano-size of the crystallites. The background signal is induced by air and the polymer substrates used for the PXRD measurement.

## Details on NMR Experiments Presented

### **Figure 1: oleate-capped ZB-CdSe NPLs**

Approximatively 2 mg of oleate-capped CdSe NPLs in TCE (12.7  $\mu$ L) were mixed with 6.3  $\mu$ L 50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (30 nm pore size) was impregnated with the radical-NPL solution and then packed into a 3.2 mm sapphire rotor.

#### **Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	21
Recycle delay (s)	5.6
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 2: oleate-capped ZB-CdSe QDs**

15  $\mu\text{L}$  of saturated oleate-capped ZB-CdSe QD solution in TCE were mixed with 7.5  $\mu\text{L}$  50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (15 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for conventional <sup>113</sup>Cd 1D DNP NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-CPMG
Number of scans	4096
Recycle delay (s)	3.4
Spectral width (kHz)	333
Spinning frequency (Hz)	10000
Acquisition length (number of points)	8096
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	7.5
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 180° pulse width [ $\pi$ ] ( $\mu\text{s}$ )	8

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	32
Recycle delay (s)	3.4
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 2: oleate-capped CdSe/CdS core/shell QDs, thin shell**

12.7  $\mu\text{L}$  of saturated oleate-capped CdSe/CdS core/shell QDs (thin shell) in TCE were mixed with 6.3  $\mu\text{L}$  50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (15 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for conventional <sup>113</sup>Cd 1D DNP NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-CPMG
Number of scans	512
Recycle delay (s)	11.7
Spectral width (kHz)	333
Spinning frequency (Hz)	10000
Acquisition length (number of points)	8096
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	7.5
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 180° pulse width [ $\pi$ ] ( $\mu\text{s}$ )	8

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	12
Recycle delay (s)	11.7
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 2: oleate-capped CdSe/CdS core/shell QDs, medium shell**

12.7  $\mu\text{L}$  of saturated oleate-capped CdSe/CdS core/shell QDs (medium shell) in TCE were mixed with 6.3  $\mu\text{L}$  50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (15 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for conventional <sup>113</sup>Cd 1D DNP NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-CPMG
Number of scans	352
Recycle delay (s)	7.3
Spectral width (kHz)	333
Spinning frequency (Hz)	10000
Acquisition length (number of points)	8096
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	7.5
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 180° pulse width [ $\pi$ ] ( $\mu\text{s}$ )	8

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	17
Recycle delay (s)	7.3
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 2: oleate-capped CdSe/CdS core/shell QDs, thick shell**

12.7  $\mu\text{L}$  of saturated oleate-capped CdSe/CdS core/shell QDs (thick shell) in TCE were mixed with 6.3  $\mu\text{L}$  50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (15 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for conventional <sup>113</sup>Cd 1D DNP NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-CPMG
Number of scans	128
Recycle delay (s)	6.0
Spectral width (kHz)	333
Spinning frequency (Hz)	10000
Acquisition length (number of points)	8096
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	7.5
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 180° pulse width [ $\pi$ ] ( $\mu\text{s}$ )	8

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	17
Recycle delay (s)	6.0
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 3: oleate-capped ZB-CdSe quantum dots (in grey)**

Approximatively 1.5 mg of oleate-capped CdSe QDs in TCE (12.7  $\mu$ L) were mixed with 6.3  $\mu$ L 50 mM TEKPol in TCE on a watch glass yielding a final TEKPol concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (30 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	16
Recycle delay (s)	5.0
Spectral width (kHz)	1667
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1900
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 3: oleate-capped ZB-CdSe NPLs (in blue)**

Approximatively 2 mg of oleate-capped ZB-CdSe NPLs in TCE (12.7  $\mu$ L) were mixed with 6.3  $\mu$ L 50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (30 nm pore size) was impregnated with the radical-NPL solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	18
Recycle delay (s)	6.8
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 4: oleate-capped core/crown CdSe/CdS NPLs**

Approximately 1.5 mg of oleate-capped core/crown CdSe/CdS NPLs in TCE (12.7  $\mu$ L) were mixed with 6.3  $\mu$ L 50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (30 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for conventional <sup>113</sup>Cd 1D DNP NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-CPMG
Number of scans	512
Recycle delay (s)	6.8
Spectral width (kHz)	385
Spinning frequency (Hz)	10000
Acquisition length (number of points)	9326
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	2.5
Contact pulse length (ms)	10.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	71
<sup>113</sup> Cd 180° pulse width [ $\pi$ ] ( $\mu$ s)	10

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	41
Recycle delay (s)	5.2
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	1.4
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 5: benzoate-capped CdSe magic-sized clusters**

To 12.7  $\mu\text{L}$  of a highly concentrated solution of benzoate-capped CdSe magic-sized cluster solution in TCE 6.3  $\mu\text{L}$  50 mM TEKPol in TCE were added to on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (7 nm pore size) was impregnated with the radical-cluster solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for conventional <sup>113</sup>Cd 1D DNP NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-CPMG
Number of scans	64
Recycle delay (s)	26
Spectral width (kHz)	667
Spinning frequency (Hz)	10000
Acquisition length (number of points)	16092
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 180° pulse width [ $\pi$ ] ( $\mu\text{s}$ )	8

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	30
Recycle delay (s)	6.8
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

**Figure 5: phosphonate-capped W-CdSe QDs**

Approximatively 5 mg of phosphonate-capped W-CdSe QDs in TCE (12.7  $\mu$ L) were mixed with 6.3  $\mu$ L 50 mM TEKPol in TCE on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (30 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for conventional <sup>113</sup>Cd 1D DNP NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-CPMG
Number of scans	32
Recycle delay (s)	5.1
Spectral width (kHz)	1667
Spinning frequency (Hz)	10000
Acquisition length (number of points)	40080
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	2.5
Contact pulse length (ms)	12.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 180° pulse width [ $\pi$ ] ( $\mu$ s)	8

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	13
Recycle delay (s)	5.0
Spectral width (kHz)	1667
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1920
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	62
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu$ s)	1.4
Number of PASS steps	6
Number of echoes	60
Number of phases	128

**Figure S2: oleate-capped ZB-CdS QDs**

To 15  $\mu\text{L}$  of saturated solution of oleate-capped CdS QD solution in TCE 7.5  $\mu\text{L}$  50 mM TEKPol in TCE were added to on a watch glass yielding a final radical concentration of 16 mM. Minimal amount of meso-SiO<sub>2</sub> (15 nm pore size) was impregnated with the radical-QD solution and then packed into a 3.2 mm sapphire rotor.

**Acquisition parameters for <sup>113</sup>Cd DNP enhanced PASS-PIETA NMR**

Magnetic field	14.1 T
Temperature	100 K
Rotor diameter (mm)	3.2
Pulse Sequence	CP-PASS-PIETA
Number of scans	16
Recycle delay (s)	8.4
Spectral width (kHz)	625
Spinning frequency (Hz)	10000
Acquisition length (number of points)	1220
<sup>1</sup> H 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	2.5
Contact pulse length (ms)	14.0
<sup>1</sup> H rf field during contact pulse (kHz)	94
<sup>113</sup> Cd rf field during contact pulse (kHz)	50
<sup>113</sup> Cd 90° pulse width [ $\pi/2$ ] ( $\mu\text{s}$ )	1.6
Number of PASS steps	12
Number of echoes	40
Number of phases	48

## References

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