

Electronic Supplementary Information

Identifying Short Surface Ligands on Metal Phosphide Quantum Dots

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Experimental

Materials: Cadmium acetate ($\text{Cd}(\text{OAc})_2$, $\geq 99.99\%$), HDA 98%, palmitic acid 99%, and tris(trimethylsilyl)phosphine ($(\text{TMS})_3\text{P}$, $\geq 98.0\%$) were purchased from Strem. tris($\text{N,N}'$ -diisopropylacetamidinato) Indium(III) was purchased from Nanomeps. Ethanol, toluene, mesitylene and pentane (RPE, Analysis grade) were purchased from Carlo Erba. All reagents and solvents were dried, distilled and degassed before use. All manipulations were carried out under argon atmosphere using Schlenk tubes and vacuum line techniques, or in glovebox.

Synthesis of Cd_3P_2 nanocrystals: In a typical low-temperature synthesis, 350.7 mg (1.521 mmol) of $\text{Cd}(\text{OAc})_2$ and 860.8 mg (3.565 mmol) of hexadecylamine (HDA) were mixed with 8 mL of toluene and loaded into a 50 mL three-necked flask. The solution was heated to 35°C and 2 mL of a $(\text{TMS})_3\text{P}$ solution (0.25 M in toluene) was injected. After injection the color of the solution changed from yellow to battle-grey. The reaction was maintained at 35°C for 24h. During the growth aliquots were sampled to monitor the reaction, at 4h, 8h and 24h. After, the Cd_3P_2 QDs were precipitated by addition of 2 x 20 mL of EtOH, centrifuged at 20000 rpm during 15 min, and dry under vacuum during 5h.

Synthesis of $\text{Cd}_3\text{P}_2\text{-OH}$ nanocrystals: 98.5 mg (0.207 mmol based on P) of Cd_3P_2 QDs were dissolved in 2 mL of toluene into a 50 mL three-necked flask. The solution was stirred at room temperature and then 37 μL (2.07 mmol) of degassed water was added. The reaction was maintained at room temperature for 24h. After the reaction time, the $\text{Cd}_3\text{P}_2\text{-OH}$ QDs were obtained after evaporation of the solvent until dryness under vacuum during 5h.

Synthesis of InP nanocrystals: 161.6 mg (0.3000 mmol) of tris($\text{N,N}'$ -diisopropylacetamidinato) Indium(III), 232.6 mg (0.9000 mmol) of palmitic acid, and 72.4 mg (0.300 mmol) of HDA were dissolved in 3 mL of mesitylene in a 100 mL Fischer Porter. Then, 2 mL of a $(\text{TMS})_3\text{P}$ solution (0.075 M in mesitylene) was injected at room temperature. After injection, the system was closed and stirred at 230°C for 21h. During that time, the color of the solution changed from pale yellow to dark red. Then, the reaction was allowed to reach room temperature. The InP QDs were precipitated by addition of 3 x 15 mL of EtOH, centrifuged at 20000 rpm during 12 min, and dry under vacuum during 5h.

Samples Characterization:

The NMR spectra in liquid state were obtained on a Bruker Avance I 500 spectrometer equipped with a 5 mm triple resonance inverse Z-gradient probe (TBI ^1H , ^{31}P , BB). ^1H NMR spectrum were recorded in CDCl_3 at 293 K. Diffusion measurements were made using the stimulated echo pulse sequence. The mixing time of NOESY experiment were set to 100ms.

Solid-state NMR experiments were recorded on a Bruker Avance III 400 spectrometer. Samples were packed into 3.2mm zirconia rotors inside a glove box. The rotors were spun at 16 or 20 kHz at room temperature. For ^1H MAS and ^{13}C DP (direct polarization) MAS experiments, small flip angle ($\sim 30^\circ$) were used with recycle delays of 5 s and 10 s. ^{31}P Hahn-echo MAS were performed with a recycle delay of 60 s. ^{13}C CP-MAS and ^{31}P CP-MAS spectra were recorded with a recycle delay of 3 s and contact times of 2 ms and between 2 ms and 4 ms respectively.

The FBCP NMR method relies on two polarization transfers: i) the ^1H magnetization of the ligands is flipped to the ^{31}P nuclei of the NPs by a CP transfer and ii) the reverse CP transfer from ^{31}P to ^1H nuclei. In both cases, the contact times were chosen to optimize the resulting ^{31}P (1st step) and ^1H (2nd step) intensities. Indeed, it has been shown on bone apatite that the ^1H - $\rightarrow$ ^{31}P (^{31}P - $\rightarrow$ ^1H) CP kinetics of OH group can strongly fluctuate depending of the OH environments notably through dipole-dipole coupling to surface water or spin-diffusion.¹ Observation of OH ^1H resonance that can have short $T_{1\rho}$ may require short CP contact times to give good signal to noise. The first CP transfer were optimized with ^{31}P CP-MAS (contact time between 0.2 ms and 8 ms) and the second CP contact (^{31}P - $\rightarrow$ ^1H) were tested between 0.1 and 4 ms. We also found that another crucial step for the success of the ^1H FBCP experiment is the effective elimination of the residual ^1H signals especially in the case of the ubiquitous long alkyl chain ligands where strong and sharp ^1H ligand resonances are present and characterized by long transversal relaxation time T_2 . This was achieved through reassessing the original FBCP NMR sequence. After the first CP transfer, the ^{31}P magnetization is then flipped back to the z direction where it evolves under the usually long longitudinal relaxation time $T_1(^{31}\text{P})$. During this time, the residual ^1H signals are eliminated by a saturation protocol. Two protocols have been proposed by Babonneau *et al.*: a saturation time composed of $\pi/2$ pulses with a time-decreasing interval² and two low power 90° phase shifted pulses that respect the HORROR condition.³ The train of two low power 90° phase shifted pulses that respect the HORROR condition³ did not lead to a sufficient saturation of the sharp alkyl chain signals (Figure S12). This is probably due to the fact that this protocol is based on reintroduction of the homonuclear ^1H dipolar interactions that are probably weak for the mobile alkyl chain. The second saturation protocol that uses a loop of $\pi/2$ pulses with a time-decreasing interval (from 30 ms to 5 ms by steps of 5 ms)⁴ gave better results, but still ineffective. In contrast, the sharp signal of the mobile alkyl chain (linewidth of about 30 Hz) could be efficiently saturated with a loop of sixteen $\pi/2$ pulses with interpulse delay decreasing from 400 ms to 25 ms by steps of 25 ms. The elimination efficiency was verified with an identical FBCP experiment where the ^{31}P RF power was set to zero. The FBCP experiment were conducted with a recycle delay of 2 s. Good signal to noise results could be obtained in less than 2 h for a full 3.2mm rotor (50 mg).

All chemical shifts for ^1H and ^{13}C are relative to TMS. ^{31}P chemical shifts were referenced to an external 85% H_3PO_4 sample. MAS NMR spectra were deconvoluted with Dmfit software.⁵

Samples for TEM analysis were prepared in glovebox by slow evaporation of a drop of the colloidal solution deposited onto a carbon-covered copper grid. TEM analysis were performed at the "Service Commun de Microscopie Electronique de l'Université Paul Sabatier" (TEMSCAN) on a JEOL JEM 1400 electron microscope operating at 100kV with a point resolution of 4.5 Å. The size distributions were determined by measuring at least 300 particles using image J software.

X-ray diffraction spectra were recorded on a MPD Pro Panalytical spectrometer using the Cu $\text{K}\alpha$ radiation. A powder of the sample was placed on a glass slide for the analysis.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (solid state samples).

UV-Visible Absorbance spectra were measured by using a Perkin Elmer lambda 35 scanning spectrometer with the sample in a 2 mm cells.

Photoluminescence (PL) spectra were recorded with excitation laser centred at 402 nm (Nichia-NLVH 3000E). The light is then dispersed by a monochromator PI Acton SpectraPro 2500i. The detection is done 90° by CDD camera (Spec-10:100 BR/LN). Acquisition is performed by Winspec32 software.

Analysis of Cd_3P_2 NCs:

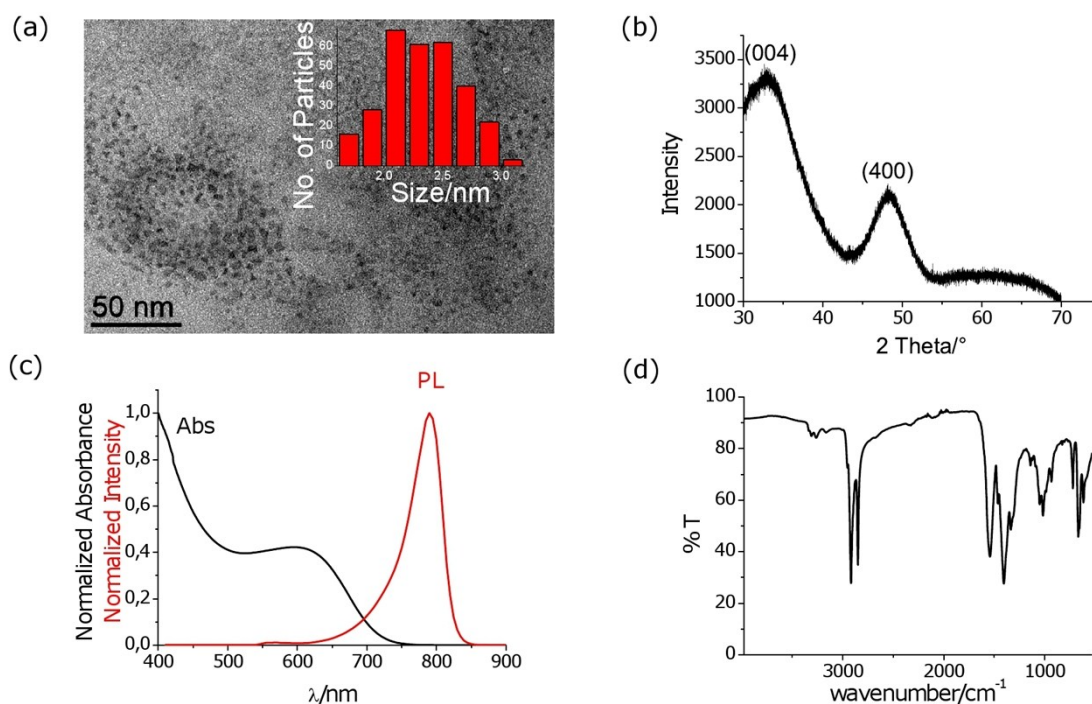


Figure S1: (a) TEM image, (b) X-ray diffractogram, (c) UV-vis and PL spectra, and (d) Attenuated Total Reflectance (ATR)-IR spectrum of Cd_3P_2 QDs. The inset of panel (a) shows the size distribution of the QDs

^{31}P Hahn-echo MAS and ^{31}P CP-MAS NMR analysis of Cd_3P_2 QDs. The ^{31}P CP-MAS (red spectrum) showed only one sharp signal around -250 ppm corresponding to ^{31}P in the immediate proximity of the Cd_3P_2 NC surface (Figure S2).

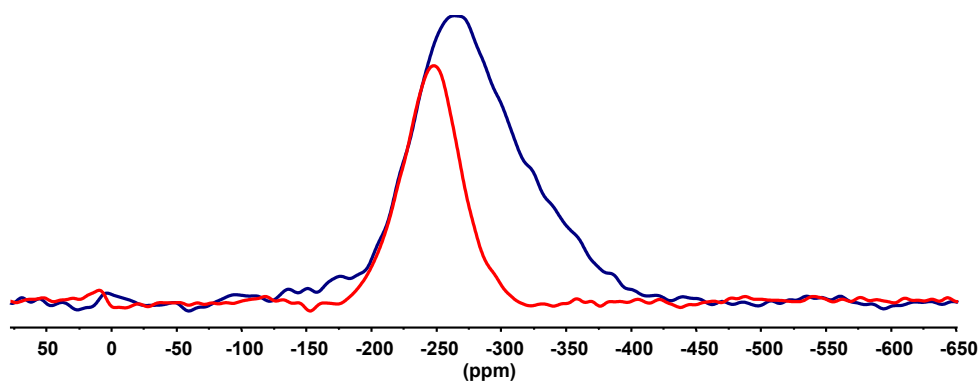


Figure S2: Comparison between ^{31}P Hahn-echo MAS (blue) and ^{31}P CP-MAS (red) NMR spectra of Cd_3P_2 QDs.

A broad resonance was observed in the ^{31}P Hahn-echo MAS NMR spectrum (blue) that was deconvoluted (Figure 1a) in two broad signals at -259 ppm (linewidth of 9.5 kHz) and -286 ppm (linewidth of 20 kHz) with a 30/70 ratio. The line shape of these resonances are much broader and more shielded than the corresponding resonances in the bulk Cd_3P_2 (-140, -162 and -178 ppm).^{6,7} This increased broadening is due to a distribution of chemical shifts which may vary with the depth of the P atoms in the NC⁸ and with the bonding environment (nature and bonding mode of capping ligand).⁹

^{13}C DP- MAS and ^{13}C CP-MAS NMR analysis of Cd_3P_2 QDs.

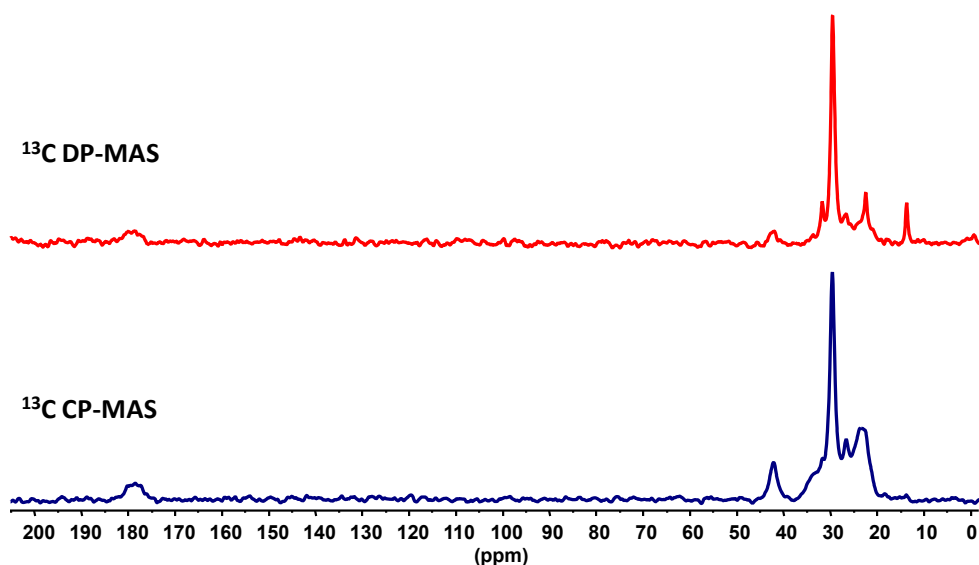


Figure S3: Comparison between ^{13}C DP- MAS and ^{13}C CP-MAS NMR spectra of Cd_3P_2 QDs.

The signal of the methyl group of HDA (13.8 ppm) is absent from the ^{13}C CP MAS NMR spectrum but can be observed in the ^{13}C with Direct Polarization (DP) MAS NMR one (Figure S3). The absence of the ^{13}C CP MAS signal of the methyl group can be explained by an averaging to zero of the ^1H - ^{13}C dipolar coupling¹⁰ indicating that the HDA alkyl chain is quite mobile at the methyl terminus. Using the ^{13}C DP MAS spectrum, the relative quantity of the ligands can be assessed from the 42.4 ppm and 178.7 ppm resonances which are almost in the same proportions (55% for OAc and 45% for HDA).

¹H NMR analysis of Cd₃P₂ QDs in CDCl₃.

Information concerning the dynamics of the ligands can be gained using ¹H liquid state NMR techniques. These experiments were performed on a colloidal solution of Cd₃P₂ QDs in CDCl₃. The ¹H NMR spectrum (Figure S4) shows sharp signals at 1.28 ppm and 0.90 ppm assigned to the central methylene and methyl groups of HDA. In addition, a broad resonance at 2.01 ppm and an even broader one at 2.71 ppm which can be hardly seen are assigned to signals of the methylene group located α to the amine function and to the OAc methyl group, respectively. The large linewidth of these signals indicate that the HDA and OAc ligands are strongly bonded to the Cd₃P₂ QDs. ¹H-¹H NOESY confirmed the strong bonding of the two ligands by observation of strong negative NOE cross-peaks typical of slow tumbling species (Figure S5). Furthermore, a strong NOE cross-peak between the methyl acetate and the central HDA methylene groups is observed indicating a close spatial proximity of the two ligands at the NP surface. Diffusion coefficient of $0.94 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ is measured for OAc and HDA by ¹H DOSY experiment corresponding to a hydrodynamic radius (R_h) of 4.0 nm (Figure S6) which is consistent with TEM analysis. However the DOSY experiment shows also the presence of HDA with faster diffusion coefficient down to $2.75 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ ($R_h = 1.4 \text{ nm}$) associated to more weakly bound HDA molecules in fast exchange with free HDA molecules. From this result, we can hypothesized that the broad resonance at 2.71 ppm of the methylene group located α to the amine function is mainly associated with the fastest diffusing HDA species. However this cannot be confirmed by the DOSY experiment as the fast T_2 relaxation time associated with the broad resonance at 2.71 ppm did not allowed measuring its diffusion coefficient. The easiest observation of the methyl acetate is probably associated to additional dynamic phenomena related to rotation of the methyl group that resulted in a sharper resonance.

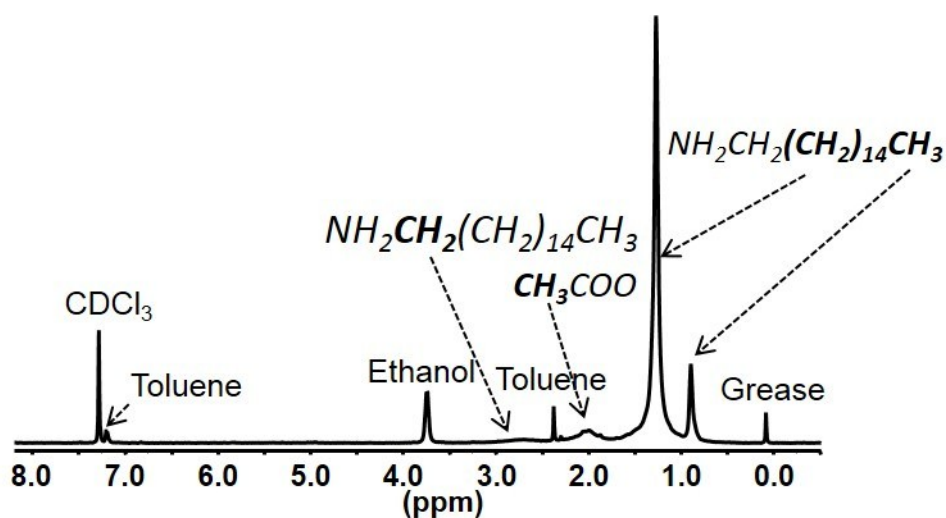


Figure S4: ¹H NMR spectrum in CDCl₃ at 293 K of Cd₃P₂ QDs.

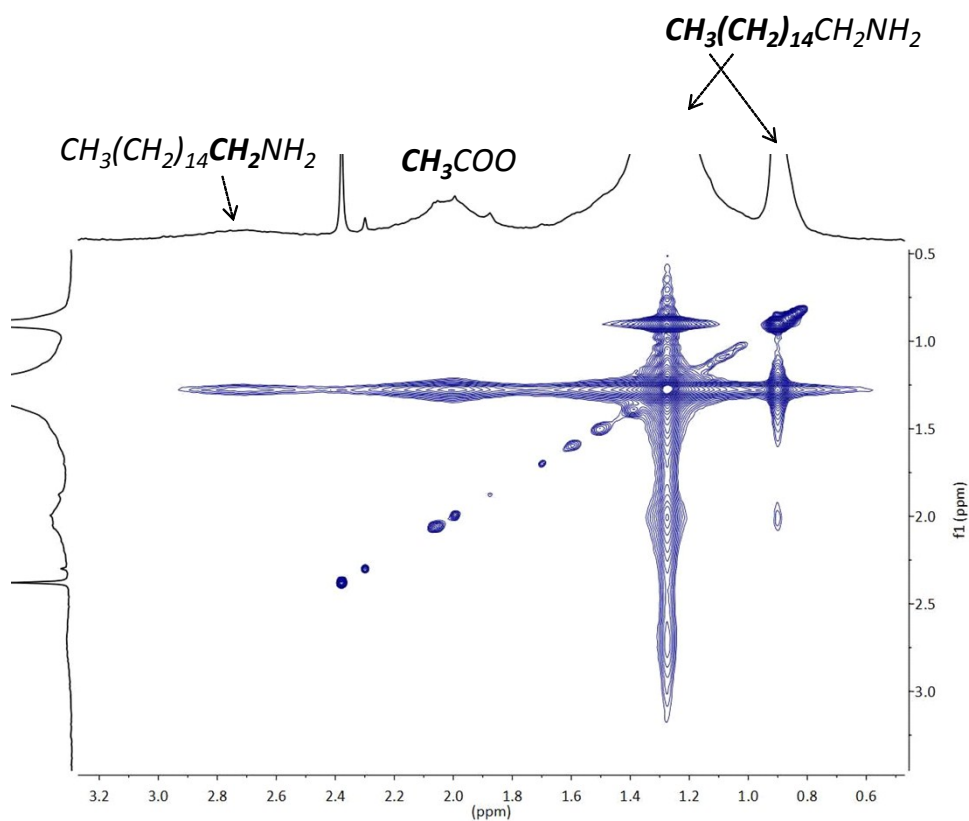


Figure S5: ^1H - ^1H NOESY NMR spectrum (mixing time 100ms) in CDCl_3 at 293 K of Cd_3P_2 QDs.

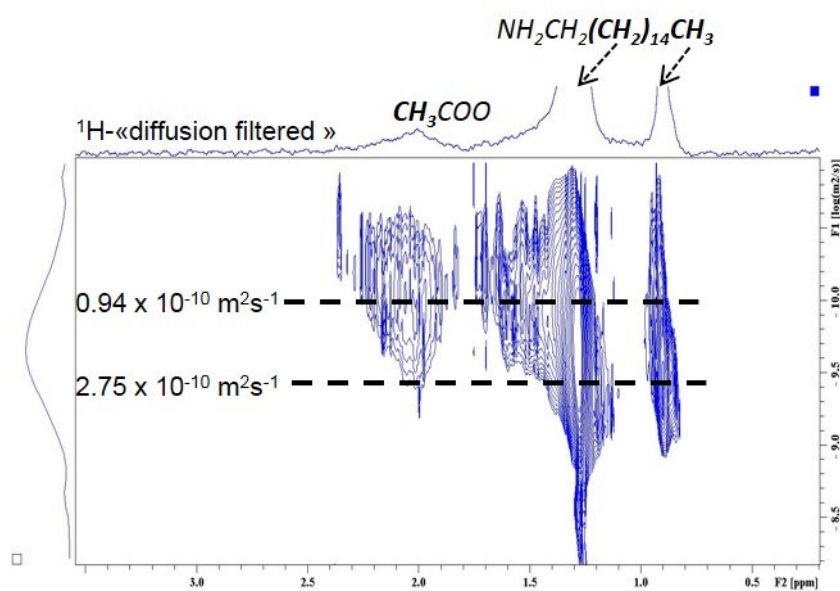


Figure S6: ^1H DOSY NMR spectrum in CDCl_3 at 293 K of Cd_3P_2 QDs. Data was processed with the CONTIN algorithm of Topspin software. The ^1H spectrum acquired with a diffusion filter to remove fast diffusing species is set on top of DOSY experiment.

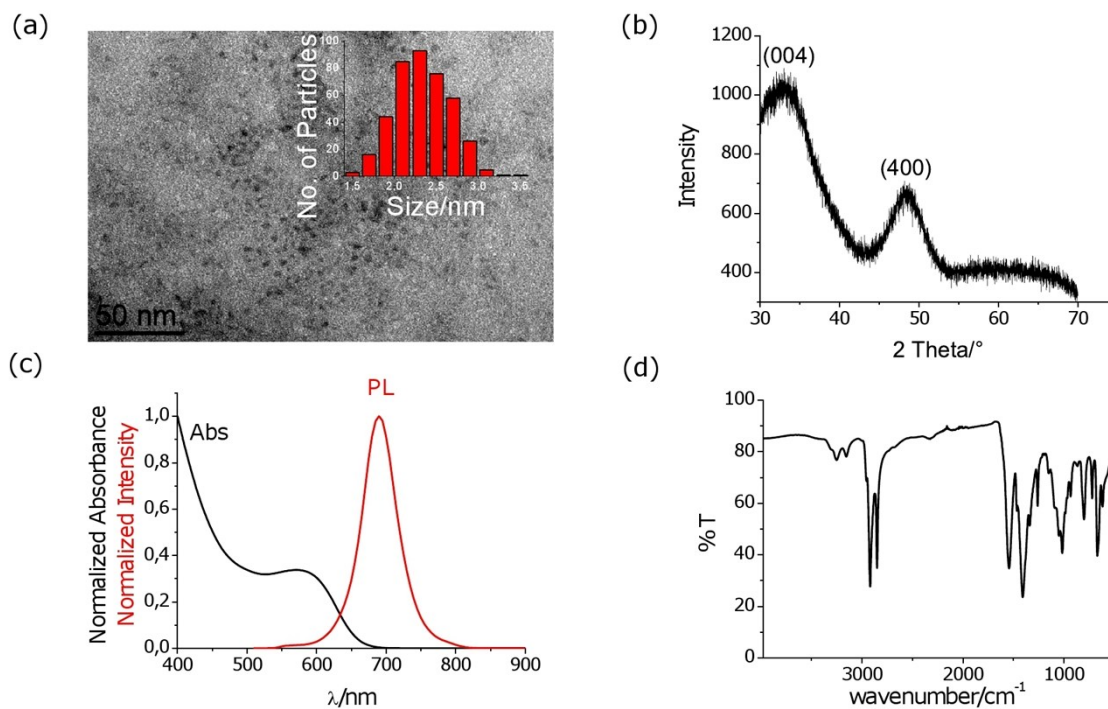


Figure S7: (a) TEM image, (b) X-ray diffractogram, and (c) UV-vis and PL spectra, and (d) ATR-IR spectrum of $\text{Cd}_3\text{P}_2\text{-OH QDs}$. The inset of panel (a) shows the size distribution of the QDs

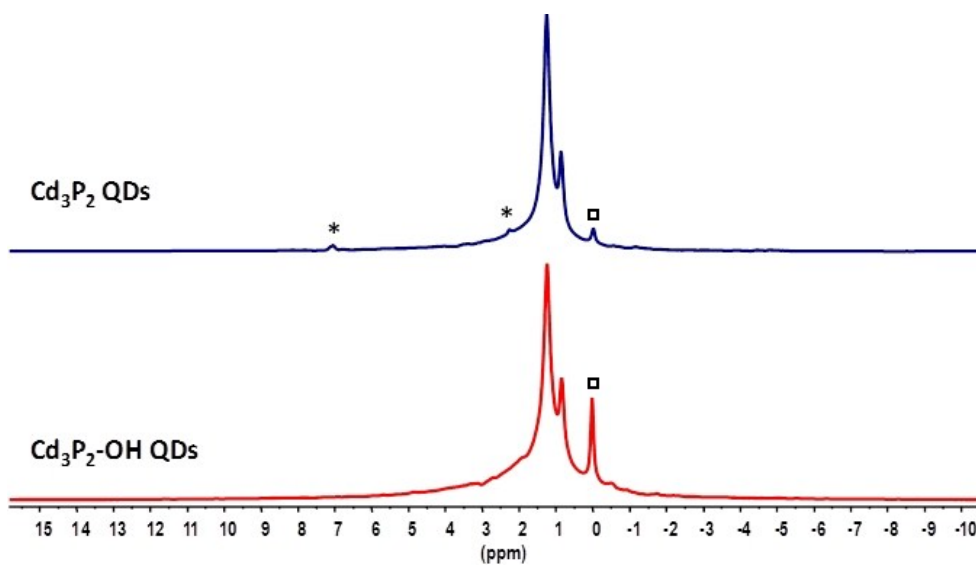


Figure S8: Comparison between ^1H MAS NMR spectra of Cd_3P_2 and $\text{Cd}_3\text{P}_2\text{-OH QDs}$, (*: residual toluene, □: grease).

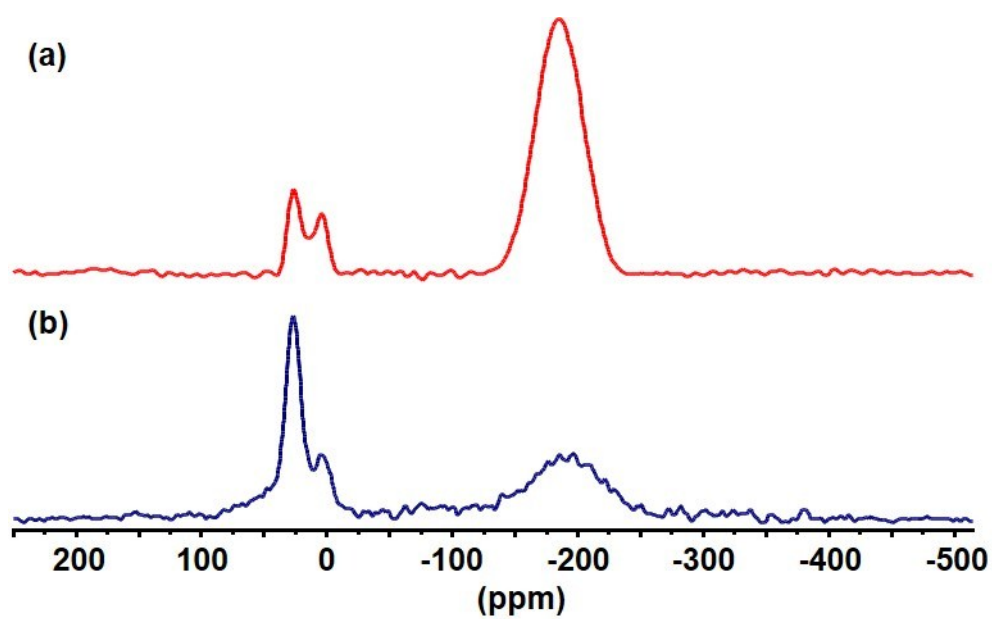


Figure S9 (a) ^{31}P Hahn-echo MAS NMR spectrum of InP QDs (spinning speed 16 kHz), (b) ^{31}P CP MAS NMR spectrum of InP QDs (spinning speed 18 kHz)

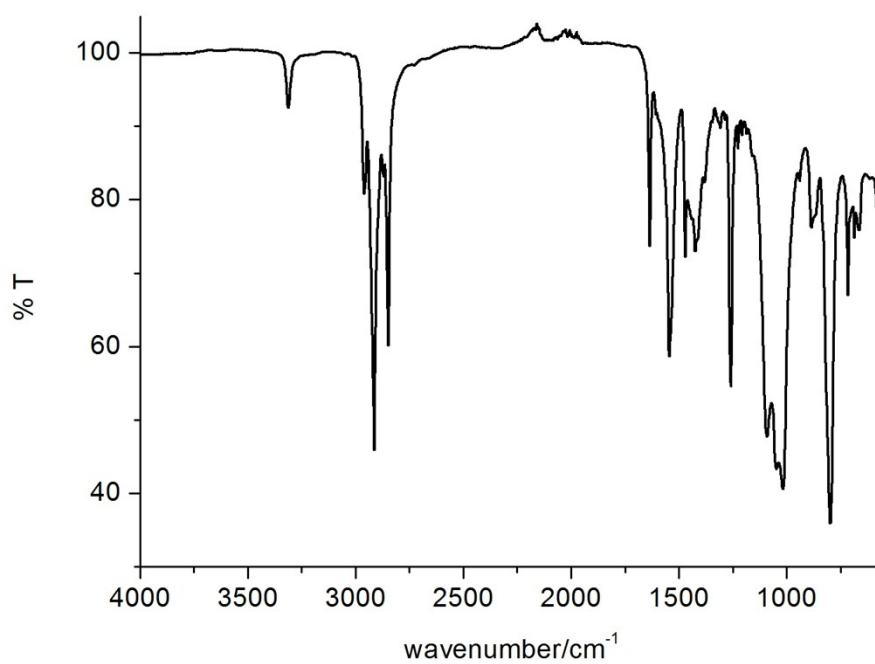


Figure S10: ATR-IR spectrum of InP QDs.

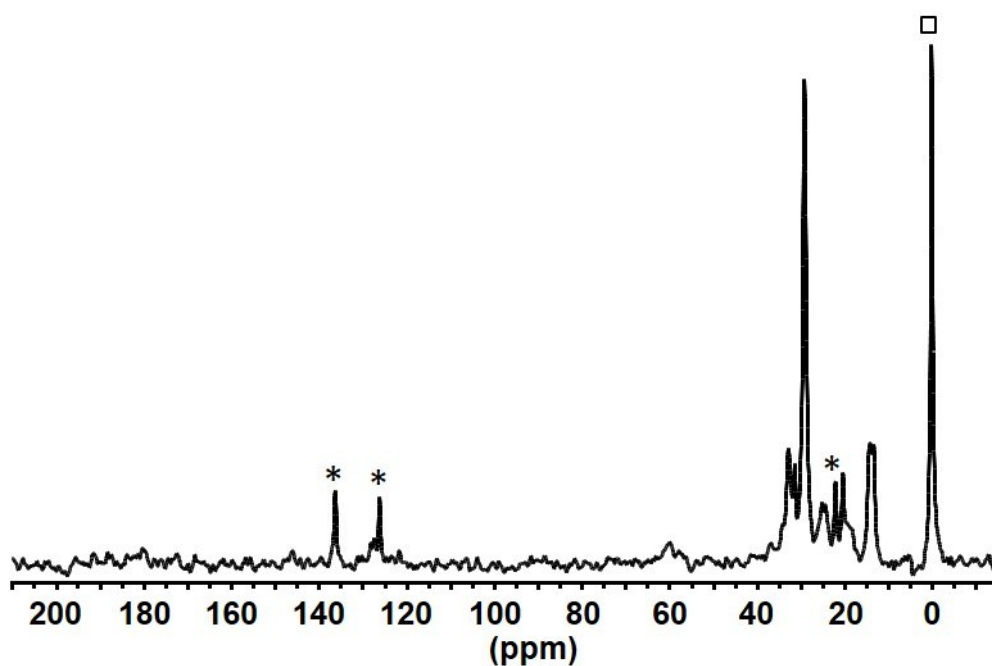


Figure S11: ^{13}C Reese MAS NMR spectrum of InP QDs (spinning speed 16 kHz). (*: residual mesitylene, $\square$: grease).

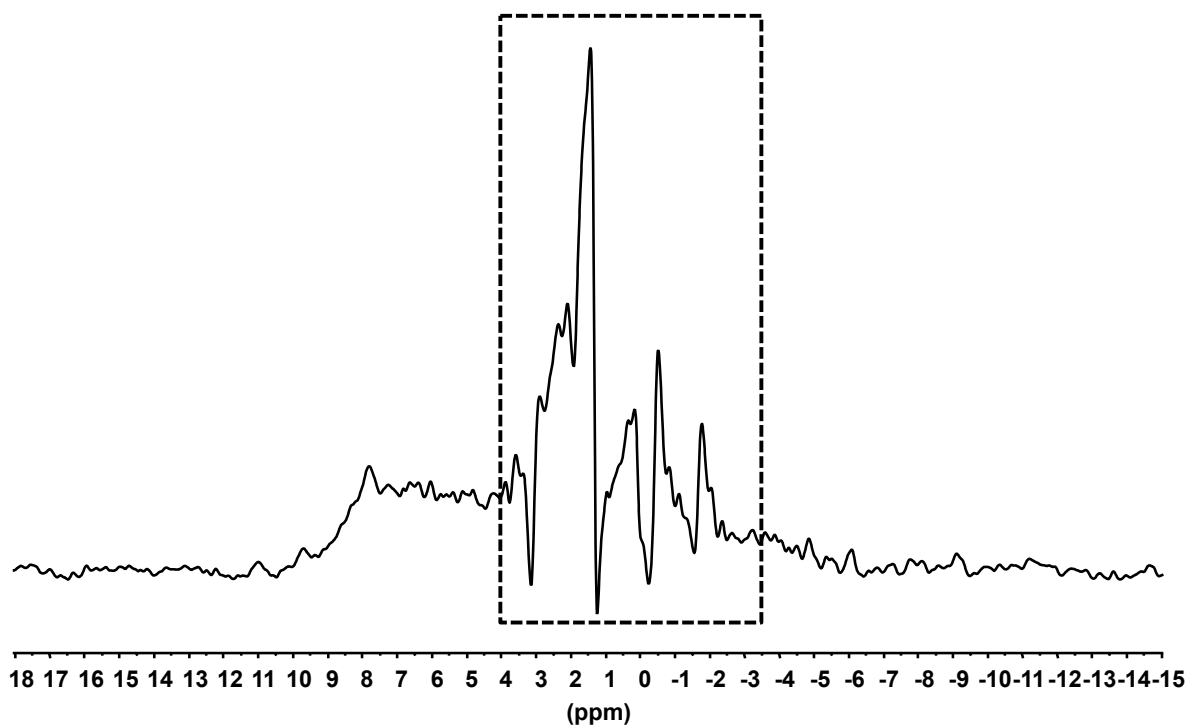


Figure S12: FBCP ^1H MAS NMR spectra of $\text{Cd}_3\text{P}_2\text{-OH}$ QDs with saturation protocol using two low power 90° phase shifted pulses that respect the HORROR condition. Signals and artefacts due to an insufficient saturation of the sharp ^1H signal of the mobile alkyl chain are clearly visible (dashed box).

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