Luminescent manganese-doped CsPbCl₃ perovskite quantum dots

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Nanocrystalline cesium lead halide perovskites (CsPbX₃, X = Cl, Br, and I) form an exciting new class of semiconductor materials showing quantum confinement. The emission color can be tuned over the full visible spectral region making them promising for light-emitting applications. Further control over the optical and magnetic properties of quantum dots (QDs) can be achieved through doping of transition metal (TM) ions such as Mn²⁺ or Co²⁺. Here we demonstrate how, following QD synthesis in the presence of a Mn precursor, dropwise addition of silicon tetrachloride (SiCl₄) to the QDs in toluene results in the formation of Mn-doped CsPbCl₃ QDs showing bright orange Mn²⁺ emission around 600 nm. Evidence for successful doping is provided by excitation spectra of the Mn²⁺ emission, with all features of the CsPbCl₃ QD absorption spectrum and a decrease of the 410 nm excitonic emission life time with increasing Mn-concentration, giving evidence for enhanced exciton to Mn²⁺ energy transfer. As a doping mechanism we propose a combination of surface etching and reconstruction and diffusion doping. The presently reported approach provides a promising avenue for doping TM ions into perovskites QDs enabling a wider control over optical and magnetic properties for this new class of QDs.

Lead halide perovskites MPbX₃ (where M = CH₃NH₃⁺, HC(NH₂)₂⁺, and Cs⁺; X = Cl, Br, and I) have recently gained interest as the result of their promising performance for a variety of optoelectronic applications, especially photovoltaics¹–³, but also light-emitting diodes (LEDs)⁴–⁵, lasing⁶–⁷, and photodetectors⁸–⁹. These materials have favorable intrinsic properties including broad absorption spectra, tunable optical spectra, high luminescence quantum yields, high carrier mobility, and long carrier diffusion length. In the past three years, a rapidly increasing number of studies were published focused on synthetic methods and morphology control of colloidal perovskites nanocrystals (NCs) aimed at improving their performance in practical applications. The hybrid organic–inorganic perovskites materials, such as CH₃NH₃PbX₃ (X = Cl, Br, and I), are outstanding solar harvesting materials in photovoltaic devices with 20% certified power conversion efficiencies¹⁰–¹¹. Sargent et al. utilized perovskites shell–capped colloidal QDs films of (PbS–CH₃NH₃PbI₃) to fabricate novel and efficient photovoltaic devices¹².

The all inorganic analogue perovskites CsPbX₃ QDs were soon after reported by Kovalenko et al.¹³. These QDs show efficient luminescence that can be tuned over the full visible spectrum (400–700 nm) by tuning of size (through quantum confinement effects) and composition (anion exchange)¹³¹⁴. Using a facile solution–based synthesis approach, cubic CsPbX₃ QDs with colorful narrow emission bands and high quantum yields of up to 90% were realized¹³. The highly efficient narrow band emission makes these QDs very useful for application in lighting and displays. For example, colloidal CsPbBr₃ QDs have been reported with efficient narrow band emission (FWHM = 86 meV; quantum yield = 90%) and reduced emission blinking making them promising for the lighting and display industry¹⁵. Interestingly, it is not generally known that this class of CsPbX₃ QDs has been known for almost 20 years. Emission and quantum confinement of CsPbX₃ QDs that form in Pb–doped CsX scintillator crystals was reported in the late 1990’s¹⁶. For the II–VI QDs such as ZnO, ZnS, ZnSe, CdS, CdSe there has been a strong effort to dope the QDs with transition metal (TM) ions such as Mn²⁺ or Co²⁺ aimed at introducing new optical and/or magnetic functionalities¹⁷–²¹. A large number of publications have reported different categories of doped QDs²²–²³. For example, efficient Mn²⁺ emission in ZnSe QDs is promising for application in solar concentrators as a result of the large spectral shift of the Mn²⁺ emission which prevents undesired reabsorption²⁵. Doping of magnetic ions in QDs also holds great promise in the field of spintronics with the possibility to dope a single magnetic ion in a single QD.
Doping can be straightforward by simply adding a dopant precursor in the reaction mixture, e.g. in ZnS:Mn$^{2+}$, but more often doping of QDs proved to be challenging$^{28}$. In the past decade new doping techniques have been developed allowing doping of systems that were previously considered not possible to dope. For example, doping CdSe with Mn$^{2+}$ was considered impossible but was later realized using a single source precursor method. More recently with diffusion doping even concentrations up to 30% Mn$^{2+}$ are now incorporated in CdSe$^{27}$. For perovskite QDs doping has only recently been realized and is highly interesting as it allows the addition of optical or magnetic functionalities to this exciting new class of material$^{26,29}$.

Here we report doping of Mn$^{2+}$ into perovskite CsPbCl$_3$ QDs (CPC–Mn) via a facile colloidal approach. A post synthesis treatment of CsPbCl$_3$ QDs prepared in the presence of Mn–stearate allows incorporation of Mn$^{2+}$. Slowly dripping a small volume (5–20 μl) of SiCl$_4$ to the dispersion of QDs in toluene results in a slow incorporation of Mn$^{2+}$ at room temperature. Evidence for successful doping is provided by a clear signature of efficient energy transfer from the CsPbCl$_3$ QD exciton to Mn$^{2+}$ ions. As Mn$^{2+}$ incorporation proceeds, the excitonic emission intensity decreases and the bright orange Mn$^{2+}$ emission increases. The excitation spectrum of the Mn$^{2+}$ emission shows all the features of the CsPbCl$_3$ QD exciton absorption. The life time of the exciton emission decreases as the Mn$^{2+}$ concentration increases as a result of fast exciton to Mn$^{2+}$ energy transfer. The proposed mechanism for incorporation involves surface etching and reconstruction and diffusion doping. Decomposition of SiCl$_4$ by trace amounts of water in the toluene yields HCl. Surface etching by H$^+$ and surface reconstruction enabled by chloride ions and Mn$^{2+}$ form a surface layer and slowly drives Mn$^{2+}$ into the QDs by ion diffusion.

The decomposition of SiCl$_4$ also gives rise to the formation of a protective SiO$_2$ layer giving a relatively high stability to the QDs. Perovskites QDs are known to degrade and show a fast loss of emission intensity under ambient conditions. The PL of the CPC–Mn QDs synthesized is relatively stable and retains over 25–30% of the maximum intensity after stirring with SiCl$_4$ for 40 days.

**Results and Discussion**

**Synthesis and characterization.** CsPbCl$_3$ QDs were prepared using a similar procedure as reported by Kovalenko et al.$^{13}$ Details on the QD synthesis and doping procedure can be found in the Methods section. In short, PbCl$_2$ and the Mn–precursor (Mn–stearate) in 1–octadecene (ODE) were dried at 120 °C after which dried oleylamine (OLAM) and oleic acid (OA) were added. The temperature was raised to 170 °C and a Cs$^{+}$ solution was added. The mixture was stirred for 1 h (red line) the formation of amorphous SiO$_2$ is evident from the broad diffraction peak of amorphous SiO$_2$ (PDF Card No. 82-1576), observed clearly from 15° to 30°. Stirring for 10 days, the pure CsPbCl$_3$ XRD patterns (black line) was still found when the precipitate (SiO$_2$) was removed by centrifuging. The lines in the XRD patterns of the QDs match the powder diffraction pattern of cubic phase CsPbCl$_3$ (Fig. S1a). The broadening of the diffraction peaks is because of the small size. The TEM image (Fig. 1b) shows the formation of monodisperse (13.1 ± 0.4 nm) side length CPC–Mn QDs and a d–spacing of 0.58 nm is clearly observed$^{23,30}$. The particle size is similar to that for samples made without Mn–precursor (Fig. S2). Figure S3 displays elemental analysis by energy dispersive X–ray spectroscopy (EDX) to confirm that Mn is present in the sample after doping, although no Mn$^{2+}$ emission is observed. Given the highly apolar nature of the Mn–precursor, the Mn–stearate can be expected to absorb in the apolar capping layer around the QDs.

In the next step a small volume of SiCl$_4$ is added to the QDs in toluene. The role of this silica precursor is twofold: it will induce the growth of protective SiO$_2$ around the QD and, more importantly, it induces the incorporation of Mn$^{2+}$ in the CsPbCl$_3$ QDs. The role of SiO$_2$ as a protective shell to protect the core material is well-known. For example, the stability of CH$_3$NH$_3$PbBr$_3$ QDs is increased when SiO$_2$ is used as a protective shell$^{31,32}$. CdSe/ZnS–SiO$_2$$^{33}$, and CdSe/CdS/ZnS–SiO$_2$$^{26,29}$, QDs were clearly improved in comparison to the uncoated QDs. The High Angle Annular Dark Field Scanning TEM (HAADF–STEM) image after addition of SiCl$_4$ and stirring for 10 days and removal of SiO$_2$ by centrifugation is shown in Fig. 1c. The monodisperse cubic particles (7.7 ± 0.5 nm) are smaller than that for the QDs before SiCl$_4$ addition. This indicates that SiCl$_4$ addition causes etching of the CsPbCl$_3$ QDs. In the HAADF–STEM images also white dots are observed. Elemental mapping (Fig. S4) reveals that these dots are highly enriched in Pb.

In the HAADF–STEM image of the sample before centrifugation both individual CPC–Mn QDs and SiO$_2$ nanoparticles were observed (Fig. 1d). This indicates that also a secondary nucleation of silica occurred and that silica was not only deposited on the QD surface in a seeded growth. EDX analysis for a region containing CPC–Mn QDs (cyan square Fig. 1d) and a region containing mainly SiO$_2$ (cyan circle Fig. 1d) are shown in Fig. 1e and f. In the EDX spectrum of the QD area (cyan square) signals of Cs, Pb, Cl, and Mn of the CPC–Mn QDs are observed and signals corresponding to Si and O are weak. The elemental analysis of the cyan circle shows strong Si and O signals, indicating the presence of a SiO$_2$ nanoparticles.

In a control experiment, SiCl$_4$ was added to the QD dispersion and then stirred for 3 days in vacuum. TEM image and EDX analysis were recorded for the CPC–Mn QDs made under vacuum are shown in Fig. S5. The CPC–Mn QDs were covered by a SiO$_2$ layer (Fig. S5a). The different SiO$_2$ morphology is ascribed to a difference in water content which determines the HCl concentration following hydrolysis of SiCl$_4$$^{34,35}$. The water present in
Toluene under ambient conditions (H₂O content ~0.06%) induces faster decomposition of SiCl₄ and silica formation. In the resulting SiO₂ covered CPC QD conglomerates all elemental signals of the CPC–Mn QDs and SiO₂ (Cs, Pb, Cl, Mn, Si, and O) were observed, as shown in Fig. S5b.

Optical spectroscopy. To monitor incorporation of luminescent dopants into QDs optical and time-resolved spectroscopy are powerful tools. When a luminescent ion is inside of a QD, fast energy transfer from the QD exciton to the dopant is expected. Absorption of light by the QD is followed by exciton→dopant energy transfer and emission from the dopant ion. Monitoring emission and excitation spectra as well as changes in the time traces of the luminescence intensity of excitonic and dopant emission provides clear signatures for the successful incorporation of a dopant in a QD. In Fig. 2a,b absorption, excitation, and emission spectra are shown for three types of CsPbCl₃ QDs: undoped QDs (CPC, no Mn added, green lines), CsPbCl₃:5%Mn QDs (CPC:5%Mn, 5% Mn–precursor added to reaction mixture, red lines) and CsPbCl₃:5%Mn–SiCl₄ (CPC:5%Mn–SiCl₄, 5% Mn–precursor added, followed by 10μl SiCl₄ and stirring for 1 day, blue lines). All three QDs show exciton emission around 400–410 nm. The emission spectra of the CPC and CPC:5%Mn samples are almost identical. For the CPC:5%Mn–SiCl₄ sample an extra emission band is observed in the red/orange spectral region around 600 nm. The excitonic emission shows a small (5 nm) blue shift and is slightly broader (halfwidth = 600 cm⁻¹ versus 550 cm⁻¹ for the CPC and CPC:5%Mn–SiCl₄ exciton emission).

The 600 nm emission wavelength is typical of the "T₁→A₁ emission from Mn²⁺. Mn²⁺ can emit in the green to deep red spectral region depending on the local coordination. The Tanabe–Sugano diagram for ions with the 3d⁵ configuration shows that the position of the emitting lowest energy excited state "T₁ shifts to lower energies as the crystal field splitting increases. In CsPbCl₃ the Mn²⁺ will substitute on the octahedrally coordinated Pb²⁺ site (the Cs⁺ site is too large). Since Cl ions are weak crystal field ligands in the spectrochemical series a green emission may be expected. However, octahedral coordination gives rise to a large crystal field splitting and even for weak ligands orange–red emission is typically observed for Mn²⁺. For example, in CdCl₃ and a variety of chloride perovskites where Mn²⁺ is in an octahedral Cl⁻ coordination, the emission maximum of the "T₁→A₁ emission of Mn²⁺ has been observed at wavelengths varying between 570 nm and 630 nm. The presently

Figure 1. Characterization of CPC–Mn QDs. (a) X-ray diffractograms of as synthesized CsPbCl₃ (1), CsPbCl₃ with added Mn²⁺–precursor (2), CsPbCl₃ with Mn²⁺–precursor after addition of SiCl₄ and stirring for 1 h (3) and 10 days (4) compared to the standard powder diffraction pattern (black vertical lines) of cubic bulk CsPbCl₃ (* marks extra peaks are caused by the silicon wafer). (b) TEM image of the CPC–Mn QDs. The inset shows a higher magnification image of a cubic particle. (c) HAADF–STEM image of the CPC–Mn QDs (after centrifuging) with SiCl₄ and stirring 10 days. (d) HAADF–STEM image of the CPC–Mn QDs (solution without centrifuging) with SiCl₄ for stirring 10 days. (e,f) EDX analysis for a CPC–Mn QDs region (cyan square) and a region without QDs (cyan circle) from Fig. 1d.
observed emission maximum at 600 nm is in excellent agreement with this range and provides further support for the assignment of the orange emission to $4\text{T}_1 \rightarrow 6\text{A}_1$ emission of Mn$^{2+}$ in an octahedral Cl$^-$ coordination.

The absorption and excitation spectra of the different CPC QDs in Fig. 2a are all similar and show an exciton peak at 410 nm. Interestingly, the excitation spectrum of the red/orange Mn$^{2+}$ emission for the CPC:5%Mn$^{2+}$SiCl$_4$ QDs (blue line) also shows the excitonic features of the QD absorption, indicating exciton-to-Mn$^{2+}$ energy transfer, a signature of incorporation of Mn$^{2+}$ in the CsPbCl$_3$ QD. Careful inspection of the emission spectra for CPC:5%Mn before SiCl$_4$ addition reveals a very weak emission feature in the orange spectral region (Fig. S6) that is not observed for the undoped CPC sample (Fig. 2b, green line). The weak Mn$^{2+}$ emission disappears after washing with acetone (see Fig. S7) and also no Mn$^{2+}$ emission was observed for acetone–washed CPC:5%Mn after addition of SiCl$_4$ under ambient conditions. This result indicates that the weak emission originates from Mn$^{2+}$ precursor adsorbed in the QD surface layer. As the Mn$^{2+}$ ions are not incorporated in the QD, energy transfer from the exciton to Mn$^{2+}$ excited states is not efficient due to the weak coupling of the exciton to remote Mn$^{2+}$ ions. Washing with acetone removes the surface absorbed Mn$^{2+}$ precursor.

As shown above, the addition of a small volume of SiCl$_4$ to the CPC QDs in toluene gives rise to Mn$^{2+}$ emission after prolonged stirring at room temperature. To study the influence of the volume of SiCl$_4$ added, emission spectra were recorded after addition of 5–20 μl SiCl$_4$ into the CPC:5%Mn QDs toluene solution under ambient conditions. The emission spectra, shown in Fig. S8, show an enhanced CPC QD exciton emission as well as Mn$^{2+}$ emission for all solutions after 12 h of stirring following SiCl$_4$ addition. The increase in PL intensity is explained by better surface passivation of the QDs and will be discussed below. The intensity of the Mn$^{2+}$ emission increases for SiCl$_4$ volumes up to 10 μl and then decreases. For the highest volumes added (15 or 20 μl SiCl$_4$) degradation of the CsPbCl$_3$ QDs was observed. As the stability of the CPC QDs is compromised, also the Mn$^{2+}$ emission intensity decreased for the highest volumes of SiCl$_4$ added. For the reaction volume used (2 ml), the optimum SiCl$_4$ amount equals 10 μl and this volume was used in subsequent experiments to follow the time evolution of Mn$^{2+}$ incorporation.

To optimize the Mn–concentration and to probe Mn–incorporation over time, extensive spectroscopic characterization was done for CPC:x%Mn–SiCl$_4$ samples taken at different times after injection of SiCl$_4$. In Fig. 3 excitation and emission spectra, luminescence decay curves of the excitonic and Mn$^{2+}$ emission as well as the integrated emission intensity ratios of Mn/QD are shown for different times (1 hour to 10 days) after injection of 10 μl SiCl$_4$ to a CPC:x%Mn QD dispersion prepared with 1, 3, 5, 7 and 10% of Mn–precursor present in the initial reaction (concentrations in mole% relative to Pb$^{2+}$). Figure 3a shows the ratio of the Mn$^{2+}$ to QD emission intensity for samples taken after 1 h to 10 days. In Fig. 3b,c photographs are shown of the QD dispersions under UV (365 nm) illumination after 1 h and 10 days of stirring. In the photographs a clear change in emission color
is observed between 1 h and 10 days. As a result of increased Mn inclusion the emission color shifts from violet to orange. Interestingly, the Mn/QD intensity ratios drastically increase after stirring for 1 day (green line). At all times, the highest Mn/QD ratio is found for a 5%Mn concentration. For higher nominal Mn-concentrations a drop in emission intensity is observed, possibly caused by concentration quenching. Concentration quenching is caused by energy transfer between dopant ions leading to migration to defects and quenching sites. Typically, this occurs at concentrations higher than 5% but as the distribution of the Mn2+ ions may not be homogeneous, a higher concentration of Mn2+ ions in the surface layer can explain a reduced luminescence intensity by concentration quenching through energy migration in a Mn-enriched surface layer. Based on this, it is concluded that the reaction conditions leading to CPC-Mn QDs with the highest Mn emission intensity is CPC:5%Mn with 10 μl SiCl4 for the reaction volume (2 ml) and QD concentrations (20 mg/ml) used here. The changes in luminescence properties over time were followed for the CPC:5%Mn SiCl4 (10 μl) system by recording excitation and emission spectra as well as luminescence decay curves of the exciton and Mn2+ emission for samples taken after 1 h, and 1, 3, 10 days. The results are shown in Fig. 3d-g.

Focusing on the CPC:5%Mn–SiCl4 (10 μl) system, the results show a continued increase in the Mn2+ emission intensity relative to the excitonic emission (Fig. 3e) for reaction times up to 10 days. The excitation spectra of the Mn2+ emission show the characteristics of the CsPbCl3 QD absorption spectrum, giving evidence for energy transfer from the QD exciton state to the Mn2+ dopant. For longer reaction times a blue shift in the first excitonic peak is observed, both in emission and excitation (Fig. 3d–e). The shift to shorter wavelengths can be explained by a decrease in the size of the QDs as a result of slow etching accompanying the Mn–incorporation process. As shown in Fig. 1 the QD size decreases from 12 to 8 nm after 10 days of stirring and this can explain the observed blue shift. The highest Mn2+ emission intensity is observed after 10 days of stirring. At longer times the intensity starts to decreases but even after 40 days a clear Mn2+ emission is observed with ~30% of the maximum emission intensity.

To gain further insight in the energy transfer process and incorporation of Mn2+ in the CPC QDs, luminescence decay curves were recorded for both the exciton and Mn2+ emission. Table 1 summarizes the lifetime (for QD exciton and Mn2+ emission) of CPC:5%Mn–SiCl4 (10 μl) for various reaction times. Energy transfer from the excitonic state to Mn2+ results in a faster exciton emission decay. The Mn2+ emission decay can be different for surface absorbed Mn2+ than for Mn2+ incorporated in the QD as energy transfer to defects or surface quenching sites is more prominent for surface Mn2+ resulting in shorter decay times for emission from surface Mn2+ ions. The luminescence decay curves were recorded for samples taken at several times during the incorporation of Mn2+ for the CPC:5%Mn–SiCl4 (10 μl) system as this was shown to give the most efficient Mn2+ emission. In Fig. 3f, the PL decay curves of the excitonic QD emission are shown. Initially, i.e. for the decay curves recorded for samples taken after 1 h to 1 day, a lengthening of the decay time is observed. The decay curve for the exciton emission from the sample stirred for 1 day is close to single exponential with a ~16 ns decay time. The initial lengthening of the decay time can be explained by improved surface passivation as a result of the chloride formation.
A remarkable increase in photoluminescence intensity and lengthening of the emission decay time was observed upon addition of phosphoric acid and explained by the removal of (surface) defect states. In addition, the exciton emission intensity strongly increases, while the excitonic emission intensity decreases. Concurrently, the exciton emission decay becomes shorter and also non–exponential (blue and violet curves in Fig. 3f). After stirring for 10 days a \( \tau_{\text{avg}} = 6.3 \text{ ns} \) decay time is observed. The shortening of the decay time is explained by energy transfer from the QD exciton state to the Mn\(^{2+}\) dopants. The non–exponential character reflects that transfer rates vary for differently doped QDs. Undoped QDs still decay with the radiative exciton decay time while QDs with one or more Mn\(^{2+}\) ions will decay with a decay rate that is the sum of the radiative decay rate and the transfer rate. The exciton–to–Mn\(^{2+}\) transfer rate will also depend on the location of the Mn\(^{2+}\) ion in the CPC–Mn QD. Transfer to a centrally located Mn\(^{2+}\) ion is expected to be faster than to a Mn\(^{2+}\) ion in the outer shell of the QD where the overlap with excitonic wavefunction is smaller.

Figure 3g show the luminescence decay curves of the Mn\(^{2+}\) emission as a function of reaction time. Long decay times in the ms time regime are observed which is typical for the spin–parity forbidden Mn\(^{2+}\) emission. Initially the decay curves are non–exponential and the faster initial decay reflects emission from Mn\(^{2+}\) at the QD surface where partial quenching by surface defect states introduces a fast non–radiative decay channel. For long reaction times (3 and 10 days) the decay is close to single exponential with a long 1.4 ms decay time suggesting that Mn\(^{2+}\) is incorporated inside the CPC host and decays with a ms radiative decay rate typical for the spin–parity forbidden Mn\(^{2+}\) emission.

Table 1. Lifetimes of QD exciton and Mn\(^{2+}\) emission of the CPC:5%Mn–SiCl\(_4\) (10 µl) for various reaction times based on a bi–exponential fit of the luminescence decay curves.

| Reaction times | Lifetime of QDs (ns) | Lifetime of Mn\(^{2+}\) (ms) |
|---------------|----------------------|-------------------------------|
| no SiCl\(_4\) | \( \tau_1 \) 2.9 9.6 7.5 | \( \tau_1 \) 2.9 9.6 7.5 |
| 1 h           | 10.3 0.5     | 10.3 0.5 |
| 1 day         | 15.6 0.2     | 15.6 0.2 |
| 3 days        | 7.5 0.7      | 7.5 0.7 |
| 10 days       | 1.3 1.4      | 1.3 1.4 |

Reaction mechanism. The synthesis procedure and characterization discussed above provide strong evidence that addition of SiCl\(_4\) to the CPC QDs in toluene in the presence of the Mn–stearate precursor results in the slow incorporation of Mn\(^{2+}\) in the CsPbCl\(_3\) QDs. It is interesting to discuss potential incorporation mechanisms and the location of the Mn\(^{2+}\) ions in the CPC QDs. Control experiments help to provide insight in the mechanism. No incorporation of Mn\(^{2+}\) was observed after thorough washing of the CPC–Mn QDs with acetone before the addition of SiCl\(_4\) (Fig. S7). This shows that the (apolar) Mn–precursor is absorbed at the CPC QD surface after the initial QD synthesis procedure in the presence of the Mn–stearate precursor. A second control experiment involves dripping of SiCl\(_4\) to the CPC QDs with Mn–precursor in toluene in vacuum. Again, no Mn–incorporation is observed under these conditions. Only the weak emission of Mn\(^{2+}\) ions around 590 nm and a faint blue emission, possibly from organic chromophores formed during ligand decomposition, were observed (Fig. S9). The absence of water prevents decomposition of SiCl\(_4\) and demonstrates that hydrolysis of SiCl\(_4\) is crucial in the reaction:

\[
\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}
\]

Hydrolysis of SiCl\(_4\) gives rise to the formation of HCl that can react with the Mn–stearate precursor (releasing Mn\(^{2+}\)) and with the CPC QD surface to both etch the surface (H\(^+\)) and reconstruct the QD surface (Cl\(^-\)). The blue shift of the excitonic emission with reaction time and the TEM images showing a decrease in particle size are consistent with the occurrence of etching of the CPC QDs. The SiO\(_2\) formed during the decomposition reaction of SiCl\(_4\) and H\(_2\)O gives rise to SiO\(_2\) spheres observed in TEM and possibly also form a thin protective SiO\(_2\) layer around the CPC QDs after prolonged reaction times. The increase of the QD exciton emission and lengthening of the exciton emission decay time in the initial hours after addition of SiCl\(_4\) signifies the positive role of the HCl in the passivation of surface defect states. Similar observations were made previously for hybrid perovskite thin films. A remarkable increase in photoluminescence intensity and lengthening of the emission decay time was observed upon addition of phosphoric acid and explained by the removal of (surface) defect states. In addition to surface reconstruction, in the presence of Mn\(^{2+}\) and Cl\(^-\) a Mn–Cl surface layer can form on the CPC QD. Etching and reconstruction of the CsPbCl\(_3\) surface can occur with the incorporation of Mn\(^{2+}\) on Pb\(^{2+}\) sites in the surface layer of the CPC QDs. Subsequent diffusion of the Mn\(^{2+}\) into the CPC QD brings Mn\(^{2+}\) inside the CPC QDs, similar to the Mn\(^{2+}\) doping of CdSe QDs through diffusion doping. Fig. 4 illustrates the proposed reaction mechanism for the incorporation of Mn\(^{2+}\) and SiO\(_2\) formation. The reaction mechanism is consistent with the long reaction times of hours to days observed for diffusion doping and cation exchange reactions at room temperature.

Further research is required to provide a more complete understanding of details on the incorporation mechanism. Based on the present experiments it cannot be excluded that the Mn\(^{2+}\) ions remain located in a surface layer of the CPC QDs. The observation of a transition from non–exponential decay to a single exponential 1.4 ms decay
of the Mn$^{2+}$ emission is important as it gives evidence that the local surroundings for the Mn$^{2+}$ ions changes during the reaction. Initially surface Mn$^{2+}$ ions are present with a shorter life time because of the proximity of surface defect states. For longer reaction times the transition to a purely exponential decay indicates the transition to the same (octahedral) coordination by Cl$^-$ for all Mn$^{2+}$ ions. This observation however does not prove that the Mn$^{2+}$ ions are homogeneously distributed through the CsPbCl$_3$ QD. The continued observation of exciton emission indicates that the transfer efficiency is limited and that the Mn$^{2+}$ ions may be preferentially situated in the surface layer where the coupling with the excitonic wavefunction is weaker. Further research on incorporation of Mn$^{2+}$ in other perovskite QDs is also interesting. For example, for CsPbBr$_3$ QDs the exciton shifts to lower energies (compared to CsPbCl$_3$) while, because of a smaller crystal field splitting for the weaker Br$^-$ ligands, the Mn$^{2+}$ emission is expected to shift to higher energies. This may lead to a cross-over between the exciton and Mn$^{2+}$ emission depending on the quantum dot size, similar to what has been observed for Mn$^{2+}$-doped CdSe quantum dots.$^{24}$

Stability. For practical application of perovskite quantum dots stability is an important issue. Thermal and photo stability are often limited for the Pb–halide perovskites and also sensitivity to moisture is serious issue that hampers the introduction of this new class of materials in products for the solar cell and lighting market$^{40-42}$. To evaluate the stability of the emission of the SiCl$_4$–modified CPC–Mn QDs solutions was followed over time. The emission intensity shows a slow decrease in intensity but retains 27% of the maximum intensity after 40 days in air, as shown in Fig. 5a. The temperature dependence of the photoluminescence was measured for CPC–Mn QDs (exciton emission) and SiCl$_4$–modified CPC–Mn QDs (Mn$^{2+}$ emission) after incorporation in a poly methyl methacrylate (PMMA) matrix. The decrease of emission intensity with temperature is shown in Fig. 5b. At 100 °C the emission of CPC–Mn QDs is completely quenched, whereas the SiCl$_4$–modified CPC–Mn QDs maintained ~50% of their initial intensity.

In conclusion, we have reported a new doping strategy for the successful incorporation of Mn$^{2+}$ ions in perovskite CsPbCl$_3$ QDs. Upon addition of SiCl$_4$ to a CsPbCl$_3$ QD/Mn–precursor dispersion in toluene incorporation of Mn$^{2+}$ occurs as demonstrated by the evolution of strong 600 nm Mn$^{2+}$ emission ($^4T_1 \rightarrow ^6A_1$) following excitation in the QD exciton states. Excitation, emission and luminescence life time measurements reveal the presence of energy transfer from the delocalized QD exciton state to the localized 3d$^6$ states of Mn$^{2+}$. The proposed incorporation mechanism involves surface etching and reconstruction by HCl formed through decomposition of SiCl$_4$ in the presence of trace amounts of water in toluene. The presently reported synthesis approach is promising for exploring other transition–metal or lanthanide ion doped perovskite QDs in order to gain a wider control over the optical and magnetic properties of doped QDs for applications in the fields of lighting and spintronics.

Methods

Preparation of Cs–oleate. The synthesis approach has been reported by Kovalenko et al.$^{13}$. In brief, Cs$_2$CO$_3$ (0.2035 g, Sigma Aldrich, 99.9%), oleic acid (0.625 ml, OA, Sigma Aldrich, 90%), and 1–octadecene (10 ml, ODE, Sigma Aldrich, 90%) were loaded into a 50 ml 3–neck flask and degassed under vacuum at 120 °C for 1 h. Subsequently, the solution was heated to 150 °C under N$_2$ for all Cs$_2$CO$_3$ reacting with OA.
Preparation of CsPbCl$_3$:x%Mn$^{2+}$ NCs

PbCl$_2$ (0.0497 g, Sigma Aldrich, 99.999%), C$_{36}$H$_{70}$MnO$_4$ (x = 5; 0.0058 g, Chemos GmbH), and ODE (5 ml) were loaded into a 25 ml 3-neck flask and degassed under vacuum at 120 °C for 1 h. Afterwards, dried oleylamine (0.5 ml, OLA, Sigma Aldrich, 70%) and OA (0.5 ml) were injected into the solution at 120 °C under N$_2$ atmosphere. The temperature was raised to 170 °C and Cs–oleate solution (0.4 ml) was quickly injected into the mixture. After the desired different reaction time, the mixture was cooled by the ice–water bath. The NCs were extracted from the crude solution through centrifuging at 3500 r.p.m. for 10 min. First, the supernatant was discarded and the precipitated particles were redispersed in toluene forming the stable colloidal solution. Second, the colloidal solution was centrifuged again, and the precipitated particles were discarded and the supernatant was redispersed in toluene forming the final solution.

Addition of silicon tetrachloride (SiCl$_4$)

Various amounts of SiCl$_4$ (Sigma Aldrich, 99%) were introduced into a 20 ml sample bottle containing 2 ml of the colloidal CPC–Mn QDs toluene solution (H$_2$O content 0.0623%)$^{31}$. After different stirring time, the white precipitates (SiO$_2$) and the transparent solutions were separated through centrifuging at 10000 r.p.m. for 10 min. In a control experiment, 10 μl SiCl$_4$ was mixed with CPC–Mn QDs (nearly water free) in a vacuum three-necked flask.

Preparation of CsPbCl$_3$:5%Mn$^{2+}$ Bulk Material

The CPC–Mn microcrystalline powder was prepared by melting starting material in an evacuated and sealed quartz ampoule$^{40}$. High-purity CsCl (Brunschwig Chemie B.V., 99.9%), PbCl$_2$ (Sigma Aldrich, 99.999%), and MnCl$_2$ (Sigma Aldrich, 99%) were mixed thoroughly and loaded into a quartz ampoule. The ampoule was evacuated and suspended with platinum wire in the high temperature region of a sintering furnace. The temperature was raised to 300 °C with a heating rate of 5 °C/min and kept for 2 h under continuous pumping to remove surface absorbed water. Then, the ampoule was sealed and the sample was sintered at 675 °C for 1 h, after which the sample was allowed to naturally cool to room temperature in the furnace.

Polymerization reaction of CPC:5%Mn$^{2+}$−SiCl$_4$ + PMMA

PMMA (0.8 g) powder was dispersed homogeneously in toluene (2 ml) for stirring 1 day. Then CPC:5%Mn$^{2+}$−SiCl$_4$ QDs (20 mg) were added into the PMMA–toluene solution and stirred for 1 day. The transparent mixture was dripped into a glass container and a copper hold, as shown in the inset of Fig. 5b. The polymerization took place under a vacuuming procedure for 1 day.
**X-ray diffraction.** XRD patterns were recorded using Cu Kα radiation (λ = 1.5418 Å) on a PW 1729 Philips diffractometer, operating at 40 kV and 20 mA. For XRD analysis, the samples were prepared by depositing the QDs colloidal solution on the silicon wafer and evaporating the solvent under vacuum atmosphere.

**Optical Characterization.** Absorption spectra were obtained using a Perkin–Elmer Lambda 950 UV/VIS/IR spectrophotometer. Excitation and emission spectra were measured by an Edinburgh Instruments FLS920 spectrofluorometer equipped with a 450 W Xenon lamp. Visible emission (400–850 nm) was detected by a Hamamatsu R928 photomultiplier tube (PMT).

**Lifetime.** Photoluminescence (PL) decay curves of the CsPbCl₃ QDs were recorded by using an Edinburgh Instruments diode laser with an excitation wavelength of 376.8 nm (65 ps pulse width, 0.2–20 MHz repetition rate) and a Hamamatsu H7422–02 PMT in combination with the Edinburgh spectrofluorometer. PL decay measurements of the Mn²⁺ dopants were done using an optical parametric oscillator (OPO) system (Opotek HE 355 II) pumped by the third harmonic of a Nd:YAG laser as excitation source and a Hamamatsu R928 PMT as light detection. The samples for optical analysis were prepared by dissolving the crude QDs production in toluene in a quartz cuvette.

**Electron Microscopy and Energy Dispersive X-ray Spectroscopy.** Scanning transmission electron microscopy (STEM) images and Energy dispersive X-ray spectroscopy (EDX) measurements were performed using a Talos™ F200X transmission electron microscope (from FEI), equipped with a high–brightness field emission gun (X–FEG) and a Super–X G2 EDX detector operated at 200 kV. TEM images were obtained using FEI TECNAI T12, operating at 120 kV. The samples for TEM imaging were prepared by depositing the QDs colloidal solution on the carbon–coated copper TEM grid and evaporating the solvent under inert atmosphere.

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Author Contributions
C.C.L. conceived the idea of the synthesis method and performed the synthesis, measurement and characterization. K.Y.X. synthesized the CPC–Mn powder and analysis. D.W. contributed to TEM measurement and analysis. A.M. revised the manuscript and supervised the project. C.C.L. wrote the first version of the manuscript and all authors discussed the results and contributed to the final version of the paper.

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