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ELECTRONIC SUPPORTING INFORMATION

"Photostability of amine-free CsPbBr₃ perovskite nanocrystals under continuous UV illumination"

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1. Time-correlated single photon counting (TCSPC) and steady-state PL experimental scheme.



Fig. S1. Scheme for the experimental setup for TCSPC and PL steady-state for long-time illumination measurements.

2. In-Situ Fourier-Transform Infrared Spectroscopy instrumental setup.



Fig. S2 (a) Photochemical cell at the FTIR accessory (frontal view). **(b)** Photochemical cell during FTIR experiment with light irradiation (top view). **(c)** Photochemical cell components (from right to left: bottom, prism, cell body, quartz window, cover, and cover screw).

3. Structural and morphological characterization using transmission electron microscopy.



Fig. S3 (a) TEM and **(b)** HR-TEM image for OA-capped CsPbBr₃ NCs, showing crystallographic fringes assigned to the lattice planes with Miller indexes (200). **(c)** Size distribution obtained from TEM images, in terms of average edge length size. **(d)** The aspect ratio data in terms of NC edge sizes, obtained from TEM images for OA-capped NCs (aspect ratio = larger edge length/smaller edge length). The aspect ratio was plotted as 2D map color scale in a (smaller edge x larger edge) surface.



Fig. S4 (a) TEM and **(b)** HRTEM image for OPA-capped CsPbBr₃ NCs, showing crystallographic fringes assigned to the lattice planes with Miller indexes (200). **(c)** Size distribution obtained from TEM images, in terms of average edge length size. **(d)** The aspect ratio data in terms of NC edge sizes, obtained from TEM images for OPA-capped NCs (aspect ratio = larger edge length/smaller edge length). The aspect ratio was plotted as 2D map color scale in a (smaller edge x larger edge) surface.

4. The determination of the dynamics of surface ligands in amine-free CsPbBr₃ PNCs under dark conditions using nuclear magnetic resonance spectroscopy techniques.

¹H 1D nuclear magnetic resonance spectroscopy (¹H 1D NMR) was performed on the PNC colloidal dispersions with different capping ligands, clearly indicating that the spectra of the capping molecules change when they are attached to the nanocrystal surface. ¹H NMR spectrum for OA-capped PNCs (Fig. S5) reveals that the presence of the (large) inorganic core results in broad, up-shifted (lower ppm values) peaks for protons attached to C2 and C18 positions; broad, down-shifted (higher ppm values) peaks for protons attached to C8, C9, C10, and C11; and on the maintenance of the original sharp peaks assigned to the unbound OA.^{1,2} Similarly, the ¹H NMR spectrum for OPA-capped NCs (Fig. S6) also exhibits some features due to the presence of the inorganic core.^{3,4} However, attributing the ¹H NMR peaks for each free- or bound-OPA ligand is more difficult than for those observed for OA-capped NCs, as the ¹H NMR peaks for bound oleylphosphate are broader than those observed for bound oleate, hindering the proper attribution without the support of other NMR techniques. For comparison, Fig. S5 and S6 illustrate typical ¹H NMR spectra for neat OA and OPA, respectively, yielding spectral features expected for free organic ligands.



Fig. S5 ¹H NMR spectra for OA-capped CsPbBr₃ PNCs and for neat-oleic acid, both suspended in deuterated benzene. (#: ODE; f: free-ligand; b: bound ligand).



Fig. S6 ¹H NMR spectra for OPA-capped CsPbBr₃ PNCs and for neat-oleylphosphoric acid, both suspended in deuterated benzene. (#: ODE; *: alkylphosphoric acid species; f: free-ligand; b: bound ligand).

Besides, an important 2D ¹H NMR called diffusion-ordered spectroscopy (DOSY) was used to estimate the differences in molecular diffusion for both bound and unbound ligands. According to the DOSY data for OA-capped NCs (Fig. S7), broad ¹H NMR peaks are attributed to the low diffusion coefficients (D = $2.0 \times 10^{-10} \text{ m}^2\text{s}^{-1}$), indicating that peak broadening is due to the presence of ligands tightly bound to the NC surface.^{5,6} Contrarily, sharp ¹H NMR peaks can be properly assigned to the higher value of diffusion coefficient (D = $9.6 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, see Fig. S8), indicating the presence of free-ligands in DOSY spectra for OA-capped PNCs. Similarly, DOSY spectrum for OPA-capped PNCs (Fig. S9) confirms that broad-shifted ¹H NMR peaks are related to the bound-OPA species (D = $1.7 \times 10^{-10} \text{ m}^2\text{s}^{-1}$), while sharp-shifted peaks are related to the free-OPA species (D = $3.4 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, see Fig. S10).

To reinforce our hypothesis of the presence of oleate and oleylphosphate ligands tightly bound to the PNC surface and free ligands in the suspension, we performed Nuclear Overhauser Spectroscopy (NOESY) for OA- and OPA-capped PNCs, as well as for neat OA and OPA (see Fig. S11a to S11d). Negative NOE cross-peaks were observed for neat OA and OPA (Fig. S11a and S11b, respectively), indicating increased rotational correlation time presented by free-OA and free-OPA molecules. On the other hand, the presence of positive NOE cross-peaks (Fig. S11c and S11d) indicates a reduced rotational correlation time due to the bound oleate and oleylphosphate species bound tightly on the surface of the NCs.^{5,6}



Fig. S7 ¹H NMR spectra for OPA-capped CsPbBr₃ PNCs and for neat-oleylphosphoric acid, both suspended in deuterated benzene. (#: ODE; *: alkylphosphoric acid species; f: free-ligand; b: bound ligand).



Fig. S8 Selected DOSY spectra for neat oleic acid (OA) in deuterated benzene.



Fig. S9 ¹H NMR spectra for OPA-capped CsPbBr₃ PNCs and for neat-oleylphosphoric acid, both suspended in deuterated benzene. (#: ODE; *: alkylphosphoric acid species; f: free-ligand; b: bound ligand).



Fig. S10 Selected DOSY spectra for neat oleylphosphoric acid (OPA)in deuterated benzene.



Fig. S11 Typical NOESY spectra for: (a) neat oleic acid (OA), (b) neat oleylphosphoric acid (OPA), (c) OA-capped CsPbBr₃ PNCs, and (d) OPA-capped CsPbBr₃ PNCs (blue correlations: positive NOE phase; red correlations: negative NOE phase). All NOESY spectra were obtained using the samples dissolved in deuterated benzene.

The ligand-surface dynamics presented by amine-free CsPbBr₃ perovskite nanocrystals can be detailed using the kinetic model stated by Fritzinger *et al.*⁷ As described in **Reaction R1**, the interaction between a unbound ligand (L) and a free site on a nanocrystal surface (NC*) yield a ligand bound to a nanocrystal surface (L-NC). Furthermore, the direct reaction (formation of L-NC bound) occurs with a reaction constant rate k_{on}, whereas the inverse reaction (formation of unbound ligands) occurs with a reaction constant rate k_{off}, also described in **Reaction R1**.

$$L + NC^* \stackrel{k_{on}}{\rightleftharpoons} L - NC \qquad (R1)$$

Analyzing **Reaction R1** from the kinetics point of view, the adsorption rate (r_{on}) is second order in terms of [L] and [NC*], while the desorption rate (r_{off}) is first-order in terms of [L-NC], being both described in **Equations S1** and **S2**, respectively. Consequently, with equations for r_{on} and r_{off} in hands, it is possible to determine the lifetime constant for the unbound-ligand ($\tau_{L-unbound}$) and bound-ligand ($\tau_{L-unbound}$), as described respectively by **Equations S3** and **S4**.⁷

$$r_{on} = k_{on}[L][NC^*] \tag{S1}$$

$$r_{off} = k_{off} [L - NC] \tag{S2}$$

$$\tau_{L-unbound} = \frac{1}{k_{on}[NC^*]}$$
(S3)

$$\tau_{L-bound} = \frac{1}{k_{off}} \tag{S4}$$

Since the entire exchange process can be described as the sum of the lifetimes of the unboundand the bound-ligands, it is possible to obtain a single exchange lifetime (τ_{exch}) for the ligands. Furthermore, we can describe the exchange constant rate (k_{exch}) defining it as the reciprocal of the exchange lifetime ($1/\tau_{exch}$), as presented in **Equation S5**.⁷

$$k_{exch} = \frac{1}{\tau_{exch}} = \frac{1}{\tau_{L-bound}} + \frac{1}{\tau_{L-unbound}} = k_{off} + k_{on} [NC^*]$$
(S5)

Finally, considering that the system defined by **Reaction S1** is in an equilibrium condition, it is possible to assume that the adsorption and desorption rates are equal ($r_{on} = r_{off}$). Consequently, the exchange constant rate can be expressed in terms of k_{off} and molar fraction of the free- and bound-ligands (x_{L-free} and $x_{L-bound}$, respectively), as described by **Equation S6**.^{7,8}

$$k_{exch} = k_{off} \left(1 + \frac{x_{L-bound}}{x_{L-unbound}} \right)$$
(S6)

Because all NMR techniques employed in both amine-free CsPbBr₃ samples suggest a molar fraction of bound-ligands much higher than the molar fraction of unbound-ligands ($x_{L-bound} \gg x_{L-unbound}$), along with the NMR signatures assigned to the low dynamics between the unbound- and bound-state for the surface ligands, it is possible to assume that adsorption rate is much higher than desorption rate ($k_{on} \gg k_{off}$). Hence, due to the reciprocal relation between the exchange rate and exchange lifetime, the tightly bound ligands tend to stay attached to the NC surface during a time much higher than the NMR time scale ($\tau_{exch} \sim \tau_{L-bound} \gg \tau_{L-unbound}$).^{7,8,6}

Finally, the hydrodynamic radius (r_{H}) of the PNCs (inorganic core with organic corona) were estimated using diffusion coefficient obtained from DOSY data.⁹ For OA-capped (r_{H} ~1.9 nm), smaller NCs are formed under the synthetic conditions in comparison with OPA-capped NCs (r_{H} ~2.2 nm). The same trend for the PNCs sizes has been measured by TEM. The difference between the numbers obtained by TEM and DOSY can be explained by the convection observed in DOSY experiments. Convection typically causes an increase in the apparent D, and therefore a reduction in r_{H} .¹⁰ In the case of neat ligands, DOSY spectra depicted in **Fig. S8** and **S10** indicate an average diffusion value for all ¹H chemical shifts assigned to the free-OA and free-OPA species, respectively, but slightly lower due to the formation of micelle structures of both ligands in nonpolar solvents.

Our findings on surface-ligand dynamics for amine-free CsPbBr₃ are very similar to those observed for oleate ligands tightly bound to the surface of PbSe NCs, as well as trioctylphosphine oxide ligands

tightly bound to the surface of InP NCs, both deeply detailed by Moreels *et al*.^{11,12} To summarize, the surface-ligands dynamics of amine-free CsPbBr₃ NCs can be depicted as in **Fig. S12**, with the molecules that present high diffusion coefficient better classified as non-interacting species.



Fig. S12 Scheme of the surface-ligand interface dynamics for amine-free CsPbBr₃ perovskite nanocrystals under dark conditions (L: organic surface ligands; x_{bound} : molar fraction of bound ligands; $x_{unbound}$: molar fraction of desorbed ligands; x_{free} : molar fraction of free (non-interacting) ligands; NC*: free site on the nanocrystal surface; k_{on} : adsorption constant rate; k_{off} : desorption constant rate). For the amine-free CsPbBr₃PNCs: $x_{L-unbound} \gg x_{L-unbound}$, and $k_{on} \gg k_{off}$.

5. The determination of the PL dynamics in amine-free CsPbBr₃ PNCs under continuous UV illumination.





Fig. S14 PLQY as a function of illumination time for (a) OA-capped and (b) OPA-capped CsPbBr₃ PNCs.

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