

Singlet Sensitization of a BODIPY Rotor Triggered by Marriage with Perovskite Nanocrystals

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Surface chemistry and quantum confinement in nanocrystals (NCs) can modulate the energy transfer efficiency between lead halide perovskite (LHP) NCs and acceptor molecules in hybrid assemblies. It is demonstrated here that colloidal CsPbBr₃ NCs capped with the oleic acid/oleylamine ligand pair act as a good singlet sensitizer of *meso*-(4-carboxyphenyl) BODIPY dye (C-BPY). The energy transfer efficiency of $\approx 85\%$ at 1×10^{-6} M is consistent with the strong binding of the BODIPY to the NC surface via the carboxylate group, as is evidenced by nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopies. A thorough analysis suggests a Förster resonance energy transfer (FRET) mechanism from the perovskite to the acceptor dye. These results provide a better understanding of the underlying interaction in perovskite–organic chromophore nanohybrids and can be employed in the design of novel harvesting assemblies.

1. Introduction

Modulation of energy transfer (ET) processes between metal halide perovskite nanocrystals (NCs) and organic chromophores remains an important goal in NC chemistry. They can participate in energy or charge transfer (CT) processes according to the excitation energy, the spectral overlap between the donor and the acceptor, and their redox potentials.^[1–4]

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In most of the reported examples, excitation of lead halide perovskite (LHP) in a hybrid LHP NC–organic chromophore assembly results in triplet energy transfer (ET) to the organic chromophore, while the singlet ET process is rarely observed.^[5]

Comparatively, for singlet fission of an excited organic chromophore, excitation energy into the lowest triplet level T₁ must be roughly half the excitation energy into the first excited singlet energy level S₁, making singlet fission thermodynamically favorable; additionally, the next triplet level T₂ must be above S₁ to make triplet–triplet annihilation endoergic. Singlet fission can be applied in the downconversion of light to overcome the thermodynamic limit for single-junction solar cells, thus reducing the thermal loss pathway.^[6]

Colloidal LHP NCs can be considered exceptional photosensitizers due to their high absorption coefficient ($\approx 10^6$ – 10^7 M^{−1}cm^{−1}),^[7] high photoluminescence (PL) quantum yield (Φ_{PL}) of up to 100%,^[8] and their bandgap energy tunability in the visible region.^[9] It is noteworthy that the NC surface chemistry not only controls the crystal size during synthesis, but it is also crucial to stabilize the NCs, favor their dispersibility and add functionality that may have implications for the interaction between the NC surface and energy-acceptor molecules.^[10] Moreover, optoelectronic and photonic applications of LHP NCs could involve a donor-bridge-acceptor CT system where organic ligands act as bridges.^[11] ET processes from CsPbBr₃ NCs to TiO₂ using three types of ligands, such as oleic acid (OA)/oleylamine (OAm), (3-aminopropyl)triethoxysilane (APTES), and naphthoic acid have revealed the bridge barrier effect on the modulation of the ET, which is of great importance for aromatic ligands.

Therefore, it is important to understand the role of the organic ligands in the ET and CT processes. Moreover, the excited-state nature of the sensitizing process between LHP NCs and organic chromophores is key to designing novel hybrid materials with potential future applications in photovoltaics and optoelectronics,^[12] as well as in energy-transfer photocatalysis. This recent application is very promising for chemical transformations, such as the isomerization of substituted stilbenes, ring-closing isomerization of diarylethene, and intermolecular [2+2] cycloaddition of acenaphthylene.^[13]

Concerning the differences between chalcogenide quantum dots and perovskite nanocrystal, first, it should be considered the atoms interaction is covalent in chalcogenide NCs while it is ionic in the perovskite NCs. This fact directly affects the interaction of the surface atoms with the ligand anchoring group or

functional moiety. In addition, the ionic character of perovskites reduces their stability toward external factors such as light, heat, and polar solvents. Moreover, perovskite NCs have high defect tolerance that allows their preparation with a 100% PL in contrast with chalcogenide NCs that need a shell to reach this value due to the low defect tolerance.^[14]

Triplet energy transfer from metal chalcogenide quantum dots (QDs), such as CdSe QDs, and BODIPY dyes can occur in BODIPY-capped QDs through charge recombination of the QD radical anion/BODIPY radical cation ($\text{QD}^{\bullet-}$ BODIPY $^{\bullet+}$) pair generated after excitation of the QD.^[15] FRET and CT pathways compete in the formation of such intermediate, while Dexter energy transfer was not competitive.

FRET efficiency between a BODIPY and CdSe QDs has been enhanced by using a coupling procedure that ensures a close distance between the donor and the acceptor.^[14] Moreover, 3,5-dithiophene-substituted aza-BODIPY bound to the surface of CdSe QDs self-assembled with a 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-*N*-[folate(polyethylene glycol) (DSPE-PEG-FA), thus providing an effective near infrared photosensitizer for fluorescence imaging and photodynamic therapy of tumor cells.^[16]

However, it must be considered that surface chemistry on perovskite NCs is different from that of chalcogenide NCs, where L-type ligands (neutral donors) strongly interact with the cations of the NC surface. In the case of perovskites, X-type ligands, such as ammonium and carboxylate moieties, are used to passivate their surface.^[10] Consequently, we have become interested in exploring the interaction of LHP NCs with BODIPY molecules. In this work, we emphasize the use of a BODIPY rotor in a systematic study of the effect of nanocrystal size and surface chemistry on FRET-type energy transfer. There are only two examples of singlet energy transfer from perovskite NCs to dyes, specifically from CsPbBr₃ NCs to Rhodamine derivatives and Rose Bengal as acceptor molecules.^[2,3]

Here, we explore the remarkable potential of colloidal CsPbBr₃ NCs to operate as singlet sensitizers of a *meso*-(4-carboxyphenyl) BODIPY molecular rotor, specifically 8-(4-carboxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (C-BPY), and how quantum confinement and surface ligand engineering can modulate their efficiency in the singlet sensitization and determine the localization of the acceptor chromophore. Such efficiency is systematically studied here considering the NC size, the nature of the capping ligands, and the spectral overlap integral between the donor and the acceptor. The binding of C-BPY to the NC surface is analyzed by proton nuclear magnetic resonance (¹H-NMR) and Fourier-transform infrared (FTIR) spectroscopies.

2. Results and Discussion

The interaction between the excited state of colloidal LHP NCs and C-BPY was studied by steady-state and time-resolved PL, using three different NC sizes, including confined and non-confined nanoparticles, passivated with the OA/OAm ligand pair.

The synthesis of colloidal LHP NCs was carried out following the hot-injection strategy with some modifications.^[17] Briefly, lead bromide salt was loaded into a 50 mL three-neck round bottom flask with octadecene as a noncoordinating solvent and degassed under vacuum at 100 °C. Then, the OA/OAm pair was

added to form a colorless solution. The temperature was raised to 190 °C and then cesium oleate was injected. After 5 s, the reaction was quenched through an ice/water bath and subjected to isolation/purification (see Supporting Information for further details). A series of centrifugation/decantation/redispersion steps, using methyl acetate and toluene as antisolvent and solvent, respectively, were needed to isolate three LHP NCs samples from the same batch (see Figure S1, Supporting Information, for the purification/isolation scheme). These NCs were further characterized by microscopy and optical spectroscopy.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images (Figure 1a) revealed the formation of crystalline LHP-x nanocubes, with an average edge length (x) of 5.6 ± 0.8 , 7.6 ± 1.3 , and 11.9 ± 3 nm (Figure S2, Supporting Information). HRTEM images of LHP NCs showed an interplanar distance of 4.2 Å corresponding to the crystal face (121), which is consistent with the orthorhombic crystalline phase of the perovskite.^[18,19]

The optical properties of the LHP NCs were analyzed by UV-Vis absorption and steady-state and time-resolved PL spectroscopy. The exciton peaks (Figure 1a) were observed at 494, 504, and 512 nm for LHP-5.6, LHP-7.6, and LHP-11.9, respectively, with a moderate Φ_{PL} (18–57%, Table S1, Supporting Information). The blue shifted exciton peak observed for the smaller LHP NCs was attributed to the quantum confinement effect, taking into account that the Bohr exciton diameter is ≈ 7 nm.^[17] The emission spectra showed narrow peaks (full width at half maximum of 17–21 nm) centered at 502, 510, and 520 nm for LHP-5.6, LHP-7.6, and LHP-11.9, respectively (Figure 1a, Tables S1 and S2, Supporting Information).

In order to evaluate the singlet ET between the LHP NCs and BODIPY derivatives, we chose C-BPY due to: i) the large overlap between the absorption spectrum of the dye (absorption maxima at 507 nm), and the emission spectra of the LHP NCs (502–520 nm) calculated as J integral values ($1.1\text{--}1.6 \times 10^{15} \text{ m}^{-1} \text{ cm}^{-1} \text{ nm}$),^[4] Figure S3, Supporting Information); ii) the relatively large absorption coefficient of C-BPY ($\epsilon = 2.8 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$, Figure S4, Supporting Information); iii) the low C-BPY Φ_{PL} ($\approx 1\%$), which is expected due the high degree of rotational freedom^[20,21] of the phenylcarboxylic substituent at the *meso* position of BODIPY, and iv) the presence of a carboxylic group that would facilitate the binding of the acceptor to the LHP NC surface (Scheme 1).

C-BPY was synthesized according to a reported protocol and then purified by following several cycles of chromatography and recrystallization from hexane (see Supporting Information for further details).^[22–24] The ¹H-NMR, ¹³C-NMR, and HSQC (Heteronuclear Single Quantum Coherence) spectra confirmed the structure and purity of the compound (Figures S5–S7, Supporting Information).

The emission of the LHP-x perovskite NCs in toluene ($22 \times 10^{-9} \text{ M}$) was recorded at increasing concentrations of C-BPY (from 0 up to $5 \times 10^{-6} \text{ M}$). The excitation of the NCs was chosen at a wavelength where the dye intrinsic absorption coefficient was low (about $2.5 \times 10^3 \text{ cm}^{-1}$ at 420 nm) compared to that of the LHP NCs (in the 3.1×10^6 to $37.2 \times 10^6 \text{ cm}^{-1}$ range, Figure S8, Supporting Information). Excitation at 420 nm guaranteed the selective excitation of the LHP NCs. The determination of the LHP NC concentration is described in the Supporting Information.

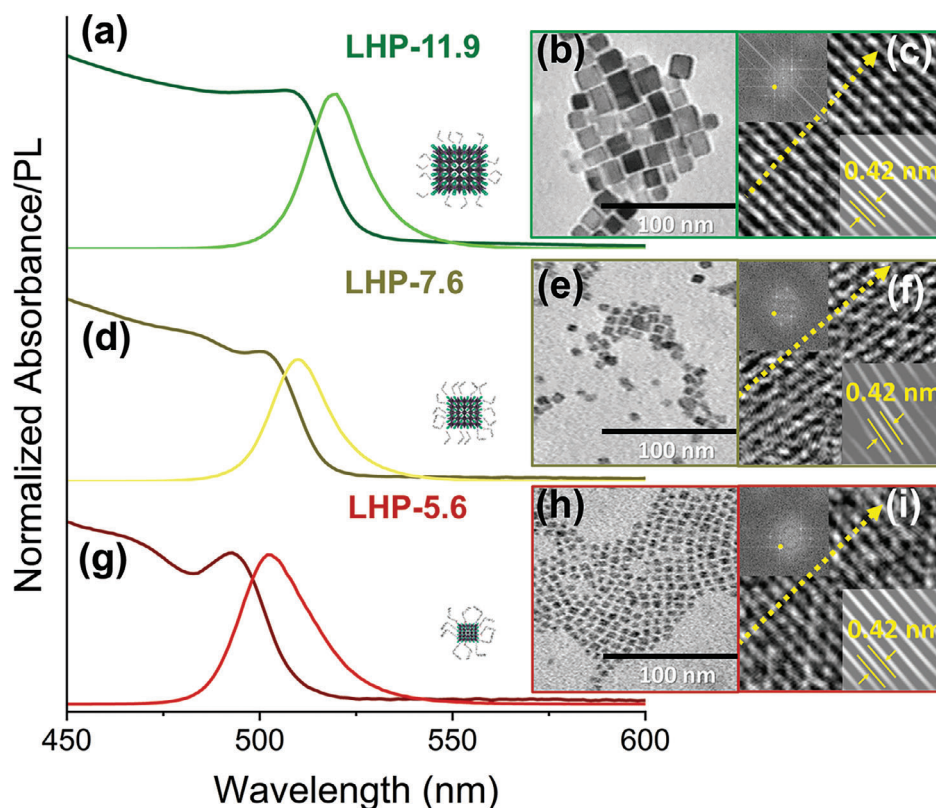
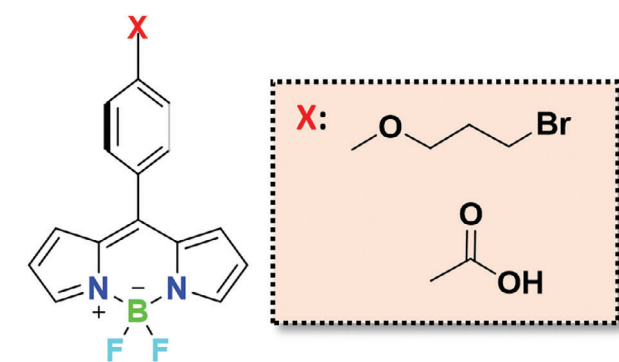


Figure 1. Normalized absorption and photoluminescence (PL) spectra (a,d,g) of LHP-*x* nanocrystals (NCs) (*x* = 5.6, 7.6, and 11.9 nm, respectively) registered under 420 nm excitation and their corresponding transmission electron microscopy (TEM) (b,e,h) and high-resolution transmission electron microscopy (HRTEM) (c,f,i) images of the three samples showing the NC morphology and the crystal plane (121) with a d-spacing of 4.2 Å. The fast-Fourier transform (FFT) of a selected nanocrystal is shown in the upper inset. The yellow dot indicates the (121) plane. The lower inset shows the region of the indicated plane (reference for Pnma space group orthorhombic CsPbBr₃ crystalline phase: COD 1533 062). The scale bar for TEM images is 100 nm.



Scheme 1. Molecular structures for BODIPY dyes used in this study; X = -O-(CH₂)₃-Br (Br-BPY); X = -COOH (C-BPY).

The emission of all the LHP NCs was quenched as the concentration of C-BPY increased (Figure 2a–c) with the concomitant emission of C-BPY in the 500–580 nm range for most of the cases, suggesting “a priori” a singlet ET between the LHP NCs and the organic chromophore as will be discussed below. The PL quenching of LHP NCs by C-BPY was analyzed by Stern–Volmer equation (Equation 1, Table 1); where *I* corresponds to the PL intensity at the emission maximum of the LHP NCs at different

concentrations of C-BPY, *I*₀ is the PL in the absence of C-BPY, *K*_{SV} corresponds to the Stern–Volmer constant and *Q* is the C-BPY concentration. It is noteworthy that *I* was corrected by the reabsorption of the emitted light from the LHP NCs by C-BPY (Figure S9 (Supporting Information) for the absorption spectrum of all LHP NCs at increasing concentrations of C-BPY; see Supporting Information for the PL correction analysis).^[25]

$$\frac{I_0}{I} = 1 + K_{SV} \cdot [Q] \quad (1)$$

A linear behavior was clearly observed for LHP NCs with *x* = 5.6 and 7.6 nm (Figure 2d). However, the data for LHP-11.9 NCs were fitted to a modified Stern–Volmer equation (Equation 2, Figure 2e); where *α* is the fraction of the initial fluorescence accessible to the quencher and *K*_α is the Stern–Volmer constant for this fraction (Table 1).

$$\frac{I_0}{I_0 - I} = \frac{1}{\alpha} + \frac{1}{\alpha \cdot K_{\alpha} (Q)} \quad (2)$$

A similar treatment was applied to the PL lifetime of the LHP NCs and fitted to a linear relationship according to Equation (3) (Figure 2f, Tables S3–S5, Supporting Information); where *K*_D is

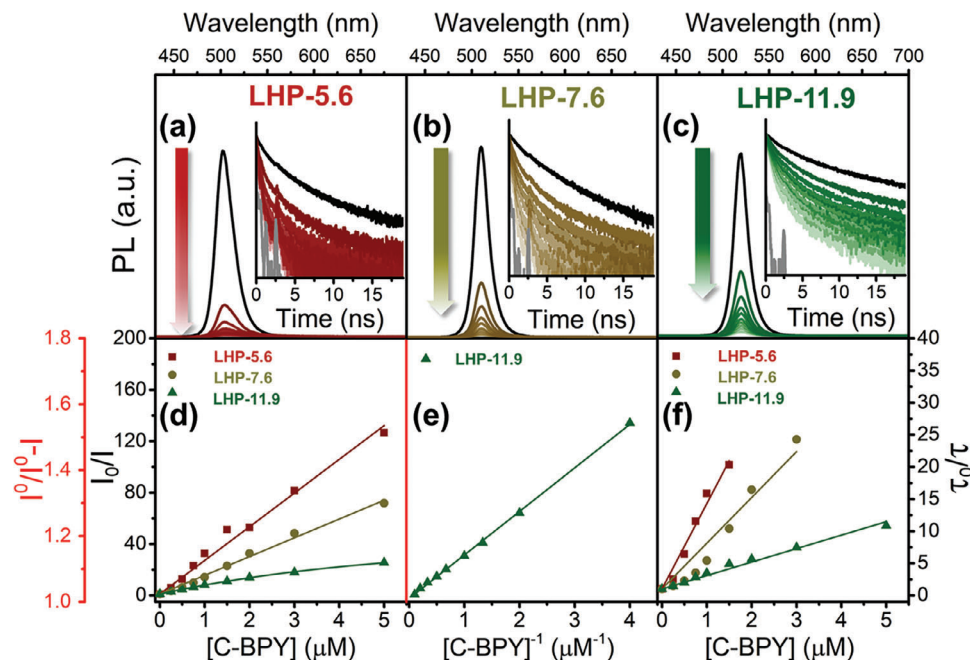


Figure 2. Photoluminescence (PL) of a toluene solution of lead halide perovskite (LHP) nanocrystals (NCs) (22×10^{-9} m) at different concentrations of C-BPY ($0-5 \times 10^{-6}$ M) recorded at 420 nm excitation wavelength for LHP-5.6 (a), LHP-7.6 (b), and LHP-11.9 (c). Inset: PL decay traces of LHP NCs with increasing concentration of C-BPY ($0-3 \times 10^{-6}$ M). Stern-Volmer (SV) plots obtained for all LHP NCs according to Equation (1) (d), Equation (2) (e), and Equation (3) (f).

Table 1. Quenching constants obtained according to Equations (1–3).

Entry	$K_{SV} [M^{-1}] \times 10^6$	$K_a [M^{-1}] \times 10^6$	α	$K_D [M^{-1}] \times 10^6$	$k_q [M^{-1}s^{-1}] \times 10^{15}$	$\Phi_Q [\%]^a$
1	26.2 ± 0.1	–	–	13.3 ± 0.6	2.6 ± 0.2	97
2	14.62 ± 0.03	–	–	7.1 ± 0.5	1.4 ± 0.1	93
3	–	7.5 ± 0.1	0.99	2.1 ± 0.1	0.11 ± 0.01	88

^{a)} The quenching efficiency was calculated at 1×10^{-6} M of C-BPY.

the Stern-Volmer constant for collisional quenching ($k_q \cdot \tau_0$), k_q is the bimolecular quenching constant and τ_0 is the PL lifetime of the NC in the absence of C-BPY (Table 1). Moreover, the quenching efficiency (Φ_Q) was calculated as $1 - (I_{obs}/I_0)$ (see Figure S10, Supporting Information). Remarkably, the quenching efficiency (Φ_Q) for LHP NCs was almost 100% at only 1×10^{-6} M of C-BPY, which is a considerably low quencher concentration when compared to that reported for Rhodamine B as a quencher of LHP NCs.^[2,26]

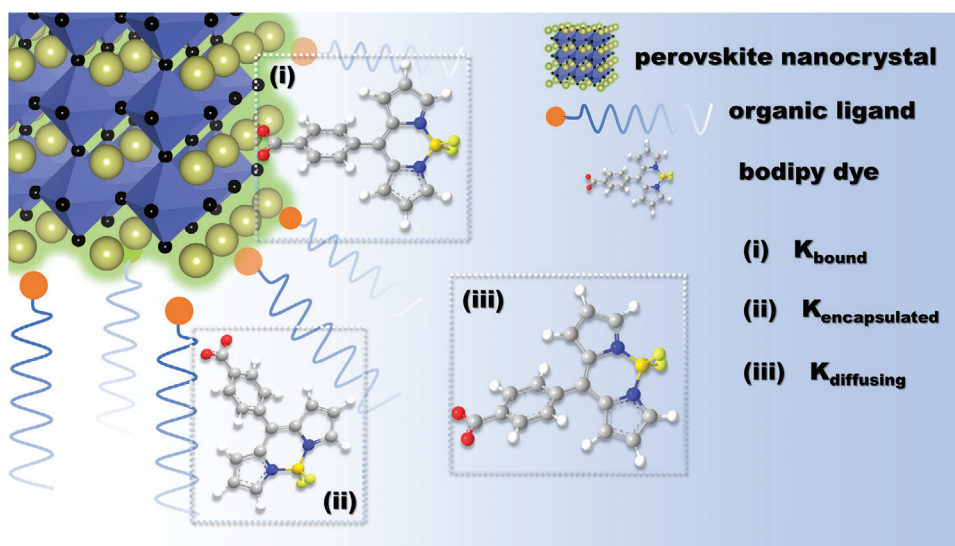
$$\frac{\tau_0}{\tau} = 1 + K_D \cdot [Q] \quad (3)$$

Analysis of the data showed a clear trend in the LHP NCs: the smaller the NC, the higher the Stern-Volmer constants for fluorescence and dynamical quenching ($K_{SV} = 26.2 \times 10^6$ M⁻¹ and $K_D = 13.3 \times 10^6$ M⁻¹ for LHP-5.6 NCs versus $K_{SV} = 14.62 \times 10^6$ M⁻¹ and $K_D = 7.1 \times 10^6$ M⁻¹ for LHP-7.6 NCs versus $K_{SV} = 7.5 \times 10^6$ M⁻¹ and $K_D = 2.1 \times 10^6$ M⁻¹ for LHP-11.9 NCs; Φ_Q of 97% versus 93% versus 88%, respectively, see Table 1, entries 1, 2, and 3, Figure S10, Supporting Information). Notwithstanding, the quenching constants for these three size-dependent nanocrystals

were still substantial. Strongly confined NCs exhibited enhanced quenching efficiency in the LHP NCs set. There are two main reasons associated with this observation: i) the higher surface/volume ratio of the smaller NCs enhances the interaction of the NCs with external agents, such as quenchers, and ii) the probability of encountering electron/hole wavefunctions at the surface increases as the NC size decreases below the Bohr radius of 7 nm^[17]; this is consistent with a higher orbital overlap between the perovskite and the chromophore.

Although this size effect was not studied in another singlet-energy transfer processes, it was clearly observed in the triplet energy transfer between LHP NCs and polycyclic aromatic hydrocarbons^[27,28]

It has to be taken into account that K_{SV} can comprise three fluorescence quenching sources: i) that related to the quenching of the LHP NC fluorescence due to the organic chromophore (C-BPY) bound to the NC surface via the carboxylic group (K_{bound}), ii) that related to the encapsulated organic acceptor, which is located within the organic ligand shell ($K_{encapsulated}$), and iii) that related to the freely diffusing chromophore acceptor in the medium ($K_{diffusing}$), see Scheme 2.



Scheme 2. Representation of the fluorescence quenching processes of LHP nanocrystals (NCs) by C-BPY (bound, encapsulated and free diffusing).

A close inspection of the quenching constant values for the LHP@OA/OAm NCs (Table 1, entry 1–3) showed that K_{SV} was approximately double the value of K_D , and the bimolecular quenching (k_q) values in the $0.11\text{--}2.6 \times 10^{15} \text{ M}^{-1}\text{s}^{-1}$ range were higher than the diffusion rate ($\approx 10^{10} \text{ M}^{-1}\text{cm}^{-1}$), thus corroborating that part of the quencher was bound to the perovskite surface (K_{bound}), or encapsulated within the organic ligand shell of the LHP/C-BPY hybrid assembly ($K_{\text{encapsulated}}$), thus facilitating the possible singlet ET from the LHP NC to C-BPY (see below).

To evaluate the role of the LHP NC surface ligands in the interaction between the perovskite and C-BPY, LHP-5.6 sample (with the highest quenching) was modified with didodecyldimethylammonium bromide (DDAB) and PbBr_2 by using the ligand exchange strategy. Shortly, a solution of DDAB (0.1 mmol) and PbBr_2 (0.2 mmol) was prepared in toluene (3 mL) by stirring and heating at 80°C . It is well known that halide vacancies in pristine LHP NCs can be passivated with the post-synthetic addition of PbBr_2 salt.^[8,29] Therefore, an aliquot of this solution (0.25 mL) was added to the pristine NCs (2.5 mg mL^{-1} in toluene) and stirred for 30 min; then, the LHP@DDAB-5.6 NCs was isolated by centrifugation in anhydrous ethyl acetate (see Figure S11, Supporting Information for further details). The size and morphology of the NCs were mostly conserved after the post-synthetic treatment (the slight reduction in the standard deviation of the average size concurred with a more homogeneous size distribution of the NCs), see Figure S12 and Table S1 (Supporting Information). Other post-synthetic approaches have been reported to enhance the stability of LHP NCs;^[30,31] however, the ligand exchange strategy with DDAB and PbBr_2 ensures effective surface passivation, thus boosting the Φ_{PL} up to about 100% by reduction of surface defects.^[32,33] Although the exciton and PL peaks of the LHP NCs remained the same after the ligand exchange process (Table S1, Supporting Information), the Φ_{PL} increased up to 97%, thus confirming the successful passivation and healing of the LHP NCs. Time-resolved PL decay trace of the LHP@DDAB-5.6 NCs fitted to a bi-exponential decay function while a tri-exponential fitting was used for LHP@OA/OAm, in-

dicating more defect-related states. The average lifetimes (τ_{av}) remained roughly the same after the ligand exchange (see Table S2, Supporting Information, for kinetic parameters to calculate the τ_{av} before and after passivation). However, the nonradiative rate constant (k_{nr}) decreased drastically from 13.4 to $0.6 \times 10^7 \text{ s}^{-1}$ after the ligand exchange. This agrees with the reduced number of nonradiative paths and the increase in the radiative rate being almost completely passivated (see values of rate constants in Table S1, Supporting Information); similar behavior has been reported elsewhere.^[34]

Comparatively, Φ_Q for LHP@DDAB-5.6 NCs was considerably lower than those of the LHP@OA/OAm-5.6 NCs ($K_{SV} = 0.7 \times 10^6 \text{ M}^{-1}$), thus proving that the nature of the ligand shell played a key role in the approach efficiency of C-BPY to the LHP NC surface (Table 1). The accessible fraction of LHP@DDAB-5.6 NCs to the quencher (0.43, Equation 2) apparently showed only static quenching (no change in the average lifetime) with a Φ_Q 4.6-fold lower than that of LHP-5.6 (Table 1, entry 1). The noticeably different behavior between the two sets of LHP NCs highlights the importance of ligand nature to facilitate the possible ET between LHP NCs and C-BPY.

To elucidate the quenching mechanism in the LHP@OA/OAm set, a thorough analysis of the emission of C-BPY ($5 \times 10^{-6} \text{ M}$) upon excitation of the LHP NCs at 420 nm was performed. A clear emission enhancement of C-BPY PL at 600 nm was observed in all the cases for the LHP NCs (Figure S13, Supporting Information), being four-, eight-, and two-fold higher than that of the control experiments (only C-BPY) for LHP-5.6, LHP-7.6, and LHP-11.9, respectively. Such enhancement could be due to the effect of both i) the occurrence of singlet ET from the LHP NC to C-BPY and ii) the possible restriction of C-BPY rotational degree of freedom when the dye was anchored to the NC surface (interaction with lead ions on the NC surface). Interestingly, the amount of the C-BPY emission showed a dependence on the pristine NC Φ_{PL} , the higher the Φ_{PL} (32%, 57%, and 18% for the smaller, medium, and larger NCs, respectively), the higher the increase of the emission.

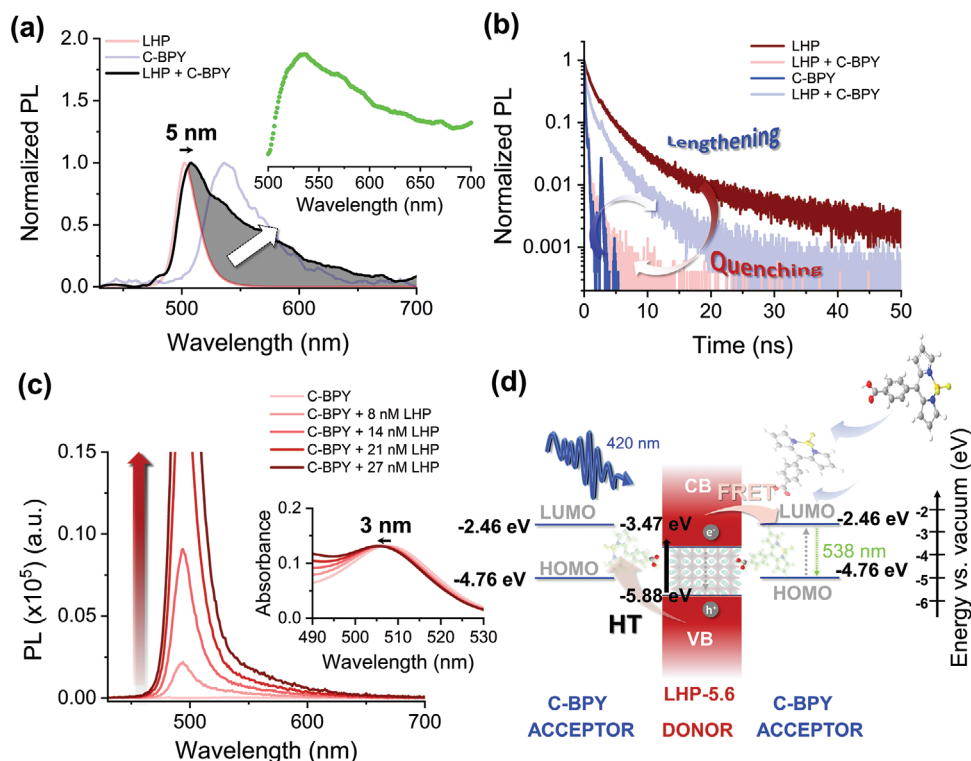


Figure 3. a) Normalized emission of LHP-5.6@C-BPY hybrid assembly compared to pristine nanocrystals (NCs) and C-BPY. Inset: the subtraction spectrum between hybrid assembly and pristine NCs. b) Normalized NCs and C-BPY lifetime decay traces were recorded at 502 and 650 nm, respectively. c) Photoluminescence (PL) spectra of C-BPY with increasing concentration of LHP-5.6 ($0\text{--}27 \times 10^{-9}$ M). d) Conduction and valence bands energy levels of the lead halide perovskite (LHP) NCs, and the HOMO–LUMO levels of C-BPY, obtained by cyclic voltammetry.

Linking of the BODIPY rotor to the NC surface and also its encapsulation within the organic capping should result in PL enhancement due to the restriction of their conformational movement, thus making the detection of BODIPY luminescence via FRET possible. The total quenching efficiency Φ_Q was dependent on the LHP NC size (Table 1). According to the experimental data, the singlet-type energy transfer from the perovskite nanocrystals to the dye was confirmed by the PL excitation (PLE) spectrum recorded at the emission wavelength of 650 nm, where the perovskite emission is null. The excitation feature of the LHP NCs was clearly observed for confined NCs and negligible for the larger NCs, indicating other mechanisms such as CT could contribute to the total quenching efficiency. Therefore, we have estimated the energy transfer efficiency by applying the methodology developed by Klinosky et al. for multiple dyes of polystyrene in microspheres.^[35] The ratio of the normalized PLE spectrum to the absorption spectrum at 10×10^{-6} M, which corresponds to the excitation energy transfer efficiency, was plotted as a function of the excitation wavelength (Figure S14, Supporting Information). The efficiency obtained from the plots at 420 nm (negligible absorption of the dye) was 85%, 70%, and 20% for the LHP-5.6, LHP-7.6, and LHP-11.9, respectively. These results agree with the larger contribution of singlet-type energy transfer mechanism for the smaller and confined LHP NCs.

However, in the case of LHP@DDAB-5.6 NCs, no sensitized emission of C-BPY was detected when the NC Φ_{PL} was $\approx 100\%$ (Figure S15, Supporting Information); this demonstrates once

again the importance of NC surface chemistry compared to NC confinement. We attribute this poor quenching efficiency and no enhancement in C-BPY emission to a low-efficient, long-range energy transfer process from the perovskite to C-BPY, since owing to the large surface area/volume ratio of these small-sized NCs, there is a high density of ligands on the surface that prevent the C-BPY from approaching its surface and, therefore, remain in solution ($K_{diffusing}$). Thus, upon energy transfer, the acceptor excited state is quickly deactivated by the nonradiative pathway as the intrinsic way ($\Phi_{PL} \approx 1\%$), which justifies the lack of emission enhancement.

With a view to exploring the quenching mechanism in the LHP@OA/OAm NCs set responsible for the deactivation of the emission and lifetime of the LHP NCs under study, several experiments were conducted for the LHP-5.6 NCs, which presented the highest quenching constants. The normalized emission spectra of the LHP-5.6@C-BPY hybrid assemblies were compared with that of pristine LHP NCs as illustrated in Figure 3a (black curve); a 5 nm bathochromic shift of the perovskite PL peak agrees well with close interaction between C-BPY and the LHP surface. Hence, a subtraction of the emission spectra of the hybrid assembly and the LHP-5.6 (Inset, Figure 3a) corresponded to the sensitized emission of C-BPY with a maximum of 538 nm. Furthermore, the emission at 600 nm was fourfold enhanced as discussed above (Figure S13a, Supporting Information) and the PLE spectra recorded at a wavelength of 650 nm, where only C-BPY is emissive, revealed

an increase in the 280–500 nm emission band, thus corroborating the LHP NCs sensitize the formation of the C-BPY singlet excited state by a singlet ET mechanism. A similar analysis was performed for all LHP NCs (Figure S13d,f, Supporting Information), indicating that the contribution of the perovskite in the PLE spectrum decreased with increasing size. Normalized PL kinetics of the LHP-5.6 in the presence of C-BPY (3×10^{-6} M, Figure 3b, Table S3, Supporting Information) showed also a drastic decrease in the average PL lifetime of the LHP NC (from 5.08 to 0.18 ns) with the concomitant enhancement of the C-BPY PL lifetime from unmeasured values to 2.14 ns, thus reflecting i) C-BPY sensitization by the LHP NC and ii) C-BPY PL with a lifetime longer than that of the freely diffusing dye due to restriction of C-BPY rotational degree of freedom when the dye is encapsulated within the NC organic ligand shell.^[36]

Similarly, in LHP-7.6 the C-BPY lifetime only increased to 0.87 ns (Figure S16a, Supporting Information). However, in the case of LHP-11.9, the decrease of the LHP lifetime resulted in a negligible lengthening of the C-BPY lifetime (Figure S16b, Supporting Information). This trend of the lengthening of the acceptor lifetime is consistent with the degree of perovskite contribution in the PLE spectrum of the C-BPY dye since the lifetime of the acceptor (recorded at 650 nm) is monitored by selectively exciting the perovskite. Therefore, we could attribute this to an energy transfer process.

For LHP@DDAB-5.6 NC, the C-BPY PL lifetime increased significantly to values close to that of the pristine LHP NCs, up to 3.8 ns (Figure S16c, Supporting Information). However, this occurred without practically affecting the LHP PL average lifetime, thus revealing that the C-BPY PL enhancement in them is due solely to a decrease in rotational freedom of the dye encapsulated within the NC ligand shell.

The sensitized emission of C-BPY was also proven by the enhancement of its PL as the concentration of LHP-5.6 NCs increased from 8 to 27×10^{-9} M (Figure 3c and Figure S17a,b, Supporting Information). The absorption peak of LHP NCs shifted to a shorter wavelength because of the interaction between LHP NCs and C-BPY (Inset, Figure 3c). Control experiments on the emission response of the LHP NCs at the same concentration are represented in Figure S17c,d (Supporting Information). PLE spectra recorded at 650 nm showed an increase in the 280–500 nm range with the LHP NC concentration with the clear presence of the peak at 494 nm corresponding to the LHP NC exciton. PLE and emission spectra of the LHP NCs in the absence of C-BPY in toluene were measured under the same experimental conditions and revealed a negligible emission at 650 nm. Furthermore, another control experiments were performed with 8-(4-(3-bromopropoxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (Br-BPY, Scheme 1), which lacks the carboxylic anchoring group (see Supporting Information for its synthesis and characterization). Emission quenching of LHP-5.6 NCs was negligible, thus corroborating that the carboxylic group is essential to facilitate the interaction of the BODIPY with the LHP NC surface and, consequently, the PL quenching (Figure S18, Supporting Information).

In short, the role of LHP NCs as singlet-energy sensitizers was evidenced by i) the photosensitized PL emission of C-BPY in the 500–650 nm range (Figure 3a and Figure S13, Supporting Information); ii) the contribution of LHP NC excitation in the

PLE spectrum recorded at 650 nm (Figure S13, Supporting Information); iii) the significant decrease of the LHP NC PL and lifetime with the concomitant increase of that of C-BPY PL (Figure 3b and Figure S16, Supporting Information) and iv) the enhancement of the C-BPY PL with the increasing concentration of the LHP NCs (Figure S17, Supporting Information). The results mentioned above revealed that the main factors that favor the singlet ET between LHP and C-BPY are the quantum confinement and the nature of the organic ligands that not only passivate the surface of the NCs, but also mediate the interaction of the NC with the photoactive chromophore.

The singlet ET between LHP NCs and acceptor molecules is expected to occur if the acceptor singlet energy (S_0-S_1) presents lower energy than the semiconductor band gap because it is a downhill conversion of energy.^[5] Comparing the singlet energy of the C-BPY of 2.38 eV, calculated by the intersection energy between the absorption and the emission spectra, and the band gap energy of LHP-5.6 NCs of 2.41 eV, a favorable ET is expected to occur (Figure 3d). Please note that the LHP NC valence band and the C-BPY HOMO/LUMO energy levels were obtained electrochemically (see Supporting Information for the electrochemical analysis, Figures S19 and S20 and Table S6, Supporting Information, for further details).

The possible mechanisms involved in the sensitization of C-BPY by LHP NCs, such as Förster, Dexter, and triplet–triplet annihilation upconversion, were analyzed. It is well known that triplet excited states are highly sensitive to the presence of molecular oxygen, due to the triplet nature of its fundamental state. Thus, PL emission of LHP-5.6 NCs in the presence of C-BPY (5×10^{-6} M) was recorded under aerobic and anaerobic atmospheres, and similar PL responses in both atmospheres ruled out the possible triplet–triplet annihilation upconversion processes to populate the C-BPY singlet (Figure S21, Supporting Information). Moreover, nanosecond transient absorption spectroscopy ruled out the formation of the C-BPY triplet excited state (Figure S22, Supporting Information). Direct Dexter mechanism is unlikely due to the lower value for the conduction band (-3.47 eV) compared to the LUMO energy state of C-BPY (-2.46 eV, calculated by electrochemical measurements, Figure 3d).

Based on the schematic energy level alignment between the LHP NCs and C-BPY shown in Figure 3d and the large spectral overlap between the emission of the perovskite and the absorption of the C-BPY (Figure S3, Supporting Information), a singlet Förster-type ET is proposed as a plausible mechanism to explain the quenching of the LHP NC emission. This fact agrees with the favored FRET mechanism over other energy transfer processes when the spectral overlap J value is large.^[2] Bulky ligands, such as DDA⁺, seem to limit the access of the C-BPY to the LHP NC surface diminishing the quenching efficiency. It is noteworthy that some contribution of the CT process (electron transfer from the HOMO of C-BPY to the valence band of LHP) to the quenching mechanism could be expected according to data in Figure 3d. The CT process has been previously studied between CsPbBr₃ NCs with different capping agents and a phenothiazine chromophore; the photoinduced hole transfer constant values were dependent on the surface ligands.^[37]

The high quenching constant value observed for the LHP@OA/OAm set is consistent with the strong binding of the C-BPY to the NC surface by the carboxylic group. ¹H-NMR

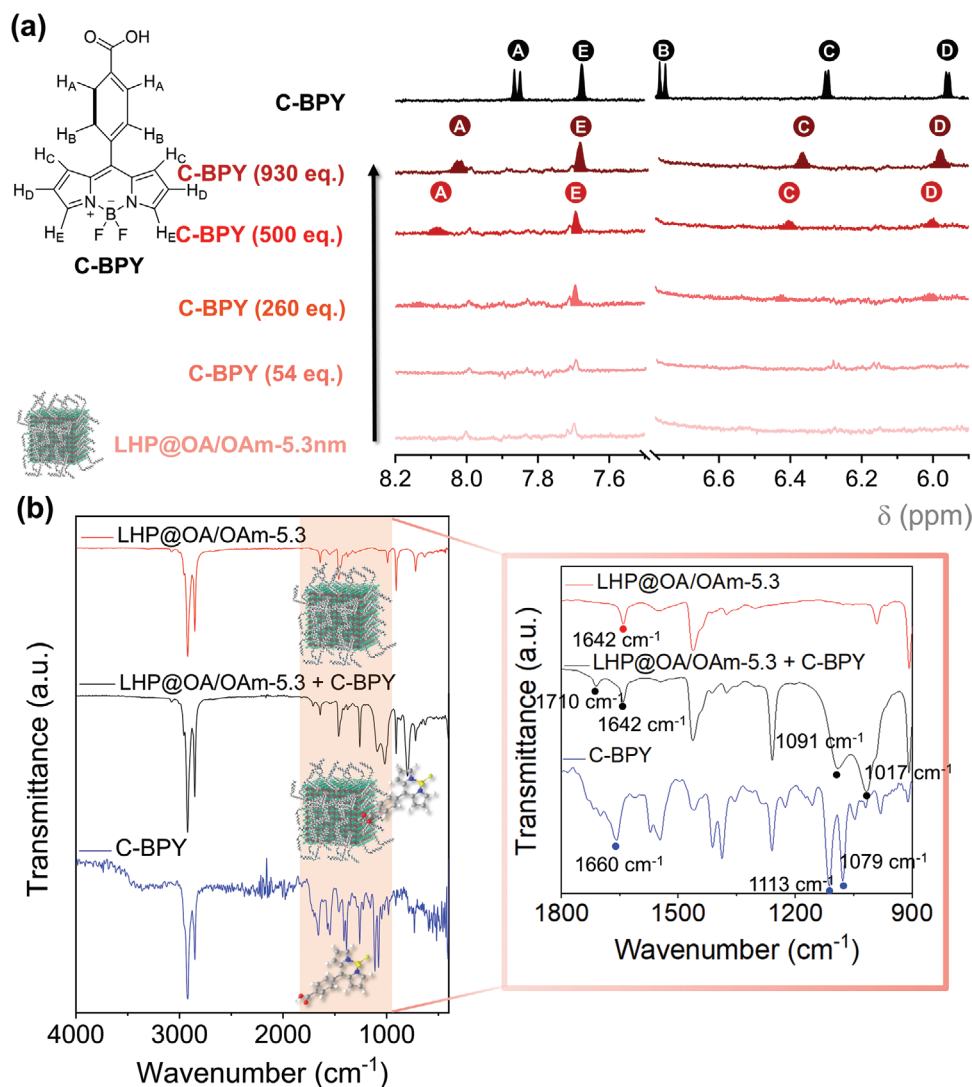


Figure 4. a) ¹H-NMR spectra of LHP-5.6 nanocrystals (NCs) (1×10^{-6} M) titration with increasing concentration of C-BPY (54–930 equivalents) and b) Fourier-transform infrared (FTIR) attenuated total reflection (ATR) spectrum of the assembly LHP-5.6 with C-BPY (5×10^{-6} M, black line) compared to the pristine LHP NC (red line) and C-BPY (blue line). Zoom region: 900–1800 cm⁻¹.

titration of the LHP-5.6 with an increasing concentration of C-BPY (54–930 equivalents) clearly showed the important down-field shift and broadening of the C-BPY proton signals, mainly those of H_A and H_C at the phenyl and indacene moieties, respectively, H_A being considerably more deshielded (Figure 4a). This finding agrees with the anchoring of C-BPY to the LHP NC surface by the carboxylic group. The ratio of 260 equivalents of C-BPY to LHP NC was close to that used for the PL analysis. Control NMR spectra were also recorded for the LHP NCs, ligands, and C-BPY (Figure S23, Supporting Information). The FTIR spectrum of C-BPY (Figure 4b) showed a broad peak in the 3500–3300 cm⁻¹ region, which can be ascribed to the acidic –OH stretching, and a strong band at 1660 cm⁻¹ ascribed to the C=O stretching of the carbonyl group. On the other hand, the FTIR spectrum of the assembly LHP-5.6 and C-BPY evidenced: i) the disappearance of the acidic –OH stretching from the phenylcarboxylic acid moiety of C-BPY, which can be attributed to the anchoring of C-BPY

to the lead cations at the NC surface via the carboxylate group and ii) the appearance of a signal at 1710 cm⁻¹ due to partial exchange of oleate from the NC surface with C-BPY (compared to the carboxylic group of oleic acid, Figure S24, Supporting Information). Strong evidence of the attachment of C-BPY to the NC surface is the drastic decrease of the intensity of the band ascribed to the C=O stretching of the carbonyl group at 1660 cm⁻¹, as well as those at about 1550 and 1400 cm⁻¹, while the two sharp C–O stretching bands at about 1100 cm⁻¹ broadened in the assembly (Figure 4b, zoom of the region 900–1800 cm⁻¹).

3. Conclusion

Surface organic ligands play a key role in the singlet sensitizing properties of the LHP NCs, passivate the NC surface, and mediate the formation of the hybrid assembly between LHP NCs and organic molecules, which combined with the quantum confine-

ment of the NCs can modulate the singlet ET process. The accessibility of the acceptor chromophore is crucial for singlet ET to proceed. Moreover, steady-state and time-resolved PL measurements enabled us to track the localization of the acceptor dye. Although surface traps in LHP NCs were passivated with the DDAB treatment, boosting near-unity Φ_{PL} , a lower quenching efficiency was obtained. These examples revealed that FRET is the operational mechanism in the PL quenching of LHP NCs by C-BPY in the hybrid LHP@C-BPY assembly. These results would be useful for designing novel light-harvesting assemblies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

BODIPY, fluorescence resonance energy transfer, perovskite nanocrystals, sensitization, singlet excited state

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