

RESEARCH ARTICLE

Surface Passivation with Lattice-Matched Bidentate Ligand Enabling High-Performance Perovskite Quantum Dot Photodetectors

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ABSTRACT

Surface halide vacancies are prevalent on lead halide perovskite (LHP) quantum dots (QDs) due to their intrinsically low formation energy, and they serve as dominant non-radiative recombination centers that degrade optoelectronic performance. While ligand exchange has been commonly used to mitigate these surface defects, the influence of multidentate ligand geometry on binding interactions with QD surfaces remains largely unexplored. In this study, we demonstrate that controlling the spatial configuration of bidentate phosphine ligands by adjusting the length of the alkyl bridge connecting the phosphorus atoms can achieve better lattice matching to the CsPbI₃ QD surface and thereby enhance ligand–surface binding strength. By comparing DPPM and DPPP, which possess distinct P–P separations, we show that the lattice-matched ligand DPPP exhibits stronger binding affinity due to improved steric compatibility with the QD lattice. As a result, DPPP-treated QDs exhibit significantly higher photoluminescence quantum yield and lower trap density than their DPPM-treated counterparts. Photodiodes incorporating DPPP-passivated QDs achieve enhanced responsivity and reduced dark current, reaching a specific detectivity of 5.67×10^{12} Jones. These findings highlight the critical role of ligand–lattice geometric matching in improving interfacial coordination and device performance, offering a new molecular design strategy for high-performance LHP QD-based optoelectronics.

1 | Introduction

Lead halide perovskite (LHP) quantum dots (QDs) have emerged as a promising class of materials for next-generation optoelectronic devices, owing to their exceptional optical tunability, solution processability, and compatibility with low-temperature fabrication processes [1–3]. LHP QDs have the chemical formula of APbX₃; typically, Cs⁺, formamidinium⁺ (FA⁺), or methylammonium⁺ (MA⁺) are used as the A cation, and halide

ions (Cl[−], Br[−], or I[−]) are used as the X anion. These materials benefit from quantum confinement effects, enabling tunable bandgaps when their sizes are reduced below the Bohr diameter [1, 4–6]. Superior optoelectronic properties of LHP QDs, such as high photoluminescence quantum yields (PLQYs), narrow emission linewidths, size- and composition-tunable emission wavelengths, and high absorption coefficients [4, 7, 8], have driven the extensive exploration of LHP QDs as active materials in diverse optoelectronic devices, including light-emitting diodes

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(LEDs), photovoltaics (PVs), and photodetectors (PDs) [2, 4, 8]. Furthermore, their solution-processability and compatibility with flexible substrates make them also suitable for large-area and wearable device applications [2, 9].

The abovementioned characteristics of LHP QDs largely originate from their defect-tolerant nature compared to classical semiconductors [1, 8]. The defect-tolerance stems from the band structure of LHP QDs, in which the majority of defect states lie within or close to the conduction or valence bands. Therefore, LHP QDs' optical and electrical properties are less vulnerable to the population of defect states compared to those of classical semiconductors, where a small population of defects can be detrimental for their optoelectronic properties [8]. Despite this advantage, the performance of LHP QD-based devices is still constrained by defects, among which A cation or halide vacancies at the QD surface are the most prevalent. Such vacancies often originate from lead-rich environment during LHP QD synthesis, or from the highly dynamic binding between surface atoms and ligands [10], which can lead to detachment of surface atoms and ligands from the QD surface during purification or processing of the QDs [1, 8]. These vacancies act as non-radiative recombination centers for excitons and trap sites for charge carriers, reducing quantum efficiencies and suppressing efficient charge transport in optoelectronic devices [1, 11]. For example, halide vacancies in LHP QDs result in uncoordinated Pb^{2+} surface sites, and the existence of these sites leads to the generation of localized electronic states near the conduction band minimum (CBM) of the QDs [12]. Therefore, mitigation of the detrimental effects of surface vacancies in LHP QDs remains a key challenge in the development of high-performance and stable LHP QD-based optoelectronic devices.

An efficient way to address this challenge is via ligand engineering. In general, the surface of as-synthesized LHP QDs is capped by ligands, typically by alkylamines and alkylacids with long alkyl chains such as oleic acid (OA) and oleylamine (OAm) [13], which passivate the surface vacancies [10, 14–17]. However, OA and OAm ligands are weakly bound to the LHP QD surface [10], so they are easily detached from the surface during solution processing or aging, leaving vacancies on the QD surface [18]. In addition, the insulating nature of their long alkyl chains is also undesirable for optoelectronic devices as it hinders efficient charge transport [19]. In this regard, ligand engineering usually aims to exchange OA and OAm ligands with other ligands with better properties, to achieve improved optical and electrical properties of the ligand-engineered LHP QDs.

Various ligand alternatives to OA and OAm have been explored. Studies have focused on achieving strong interaction between ligand molecules and LHP QD surface to ensure stable passivation of surface vacancies, and on reducing the insulating character of ligands to improve charge transport in ligand-exchanged LHP QD films. As a result of intensive research efforts, a variety of effective ligands have been reported; depending on the ligands' functional group that binds to the surface vacancy of LHP QDs, the ligands can be classified by several categories including amines/ammonium salts [20], phosphines/phosphonic acids [21], carboxylic acids [22], and organosulfur compounds [23]. One of the most promising classes among the diverse types of ligands is bidentate or multidentate ligands, which contain two

or more functional groups for binding to the QD surface. These ligands have attracted particular attention due to their ability to simultaneously coordinate with multiple vacancies on the QD surface, which offers stronger and more stable surface passivation of LHP QDs compared to their monodentate counterparts [24]. Indeed, several studies have successfully demonstrated a significant increase in the stability and PLQY of LHP QDs by introducing bidentate and multidentate ligands [25–34].

Despite the success of previous studies, there still remain questions to be addressed to fully establish the design strategy of multidentate ligands for LHP QDs. One critical molecular structural aspect of these ligands that is likely to affect their ability to coordinate with surface vacancies would be the intramolecular spatial separation between functional groups, because the functional groups need to have a proper separation distance to be simultaneously positioned at different vacancy sites. Nevertheless, little attention has been paid to how the spatial separation between functional groups in multidentate ligands affects their binding behavior and passivation efficiency on LHP QD surfaces. And consequently, the impact of this structural factor on the optoelectronic performance of LHP QD-based devices also remains largely unexplored. Considering recent literature that demonstrated the importance of precise lattice matching between the perovskite layer and underlying self-assembled monolayer in improving their interfacial stability [35], the control of intramolecular separation distance between functional groups in multidentate ligands is expected to have a significant influence on vacancy passivation and optoelectronic properties of resulting LHP QDs.

Here, we propose a lattice-matching strategy to improve the ability of the bidentate ligand to passivate the halide vacancies in LHP QDs. Among the various classes of multidentate ligands, we selected two phosphine-based bidentate ligands, 1,1-bis(diphenylphosphino)methane (DPPM) and 1,3-bis(diphenylphosphino)propane (DPPP), which are well known as coordination ligands in transition metal catalysis for carbon–carbon coupling reactions such as Suzuki, Heck, and Sonogashira cross-coupling [36]. Despite their established role in homogeneous catalysis, their use in surface defect passivation for quantum dots remains unexplored. In this study, we repurposed these ligands to investigate how the spatial separation between the two phosphorus atoms (P–P separation) influences their ability to simultaneously coordinate to adjacent halide vacancies on the QD surface. The P–P separation of bound DPPP was comparable to the lattice constant of CsPbI_3 , while the P–P separation of bound DPPM was only one-half of the lattice constant. The ligands effectively passivated the halide vacancies at the CsPbI_3 QD surface through the strong coordination of phosphorus atoms to electron-deficient and uncoordinated Pb^{2+} ions at halide vacancies. Notably, the binding energy between the ligand and QD surface was much stronger for DPPP than for DPPM, indicating that the matching of P–P separation to the lattice structure of the QDs is crucial in achieving strong surface vacancy passivation. As a result of the improved passivation, DPPP-exchanged QDs showed much higher PLQY and reduced trap densities compared to the DPPM-exchanged QDs. Furthermore, when the corresponding QD films were introduced as an active layer of photodiodes, the device incorporating DPPP-exchanged QDs exhibited greater

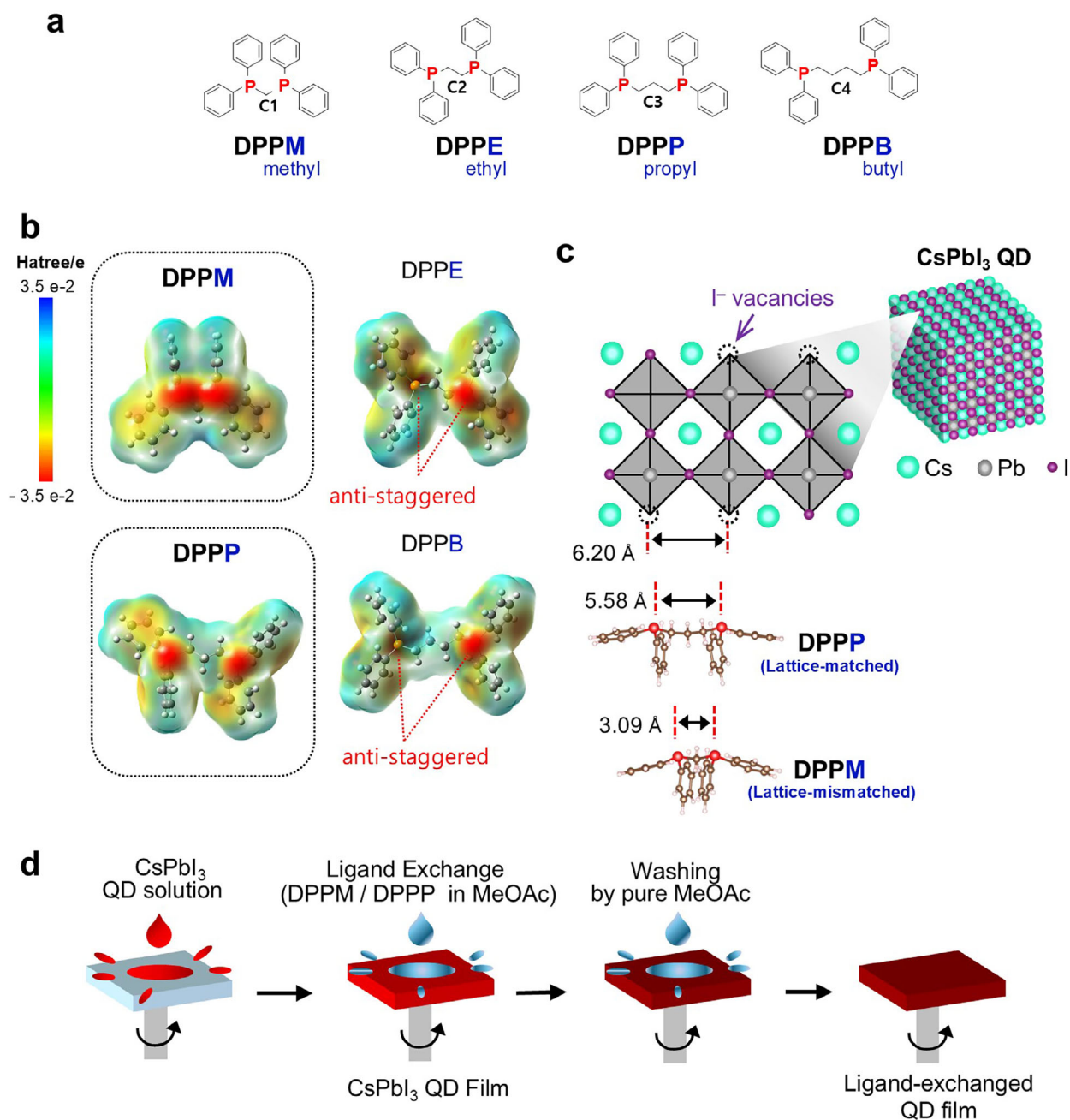


FIGURE 1 | Materials and concepts of this study. (a) Molecular structures of bidentate phosphine ligands with different linker lengths (C1–C4), controlling the P–P distance for lattice matching with CsPbI₃ QDs. (b) Energy-minimized molecular configurations of the bidentate phosphine ligands, DPPM, DPPE, DPPP, and DPPB. (c) Crystal structure of CsPbI₃ QDs and molecular structures of the ligands considered for surface passivation. The interatomic distance between the two phosphorus atoms in each ligand is controlled by varying the number of carbon atoms in the linker. DPPP results in lattice-matched alignment with the spacing between adjacent halide vacancies on the QD surface, whereas DPPM does not. (d) Schematic illustration of the postsynthetic ligand exchange process, in which the native ligands in the as-cast QD films are replaced with bidentate phosphine ligands, DPPM or DPPP, yielding DPPM-QD and DPPP-QD films.

responsivity as well as lower noise and dark currents, resulting in a high specific detectivity reaching 5.67×10^{12} Jones, which is about three times higher than the device incorporating DPPM-exchanged QDs and about an order of magnitude higher than the control device based on conventional methyl acetate (MeOAc)-exchanged QDs. This work signifies the importance of lattice matching strategy in ligand engineering for achieving highly efficient and stable LHP QD-based optoelectronic devices.

2 | Results and Discussion

2.1 | Lattice-Matched Design of Bidentate Phosphine Ligands for Halide Vacancy Passivation of CsPbI₃ QDs

Figure 1a illustrates the central idea of this study. The α -phase CsPbI₃ with a cubic crystal structure was selected as the model

LHP QD. The selection of the cubic CsPbI₃ QD was motivated by its superior stability, along with its relatively facile synthesis in achieving high crystallinity and monodispersity compared to organic-inorganic hybrid LHP QDs [18]. Furthermore, its narrow band gap makes it a suitable photoactive material for broadband photodetectors capable of detecting across the entire visible spectrum. As bidentate ligands, a series of phosphine-based ligands, DPPM, 1,2-bis(diphenylphosphino)ethane (DPPE), DPPP, and 1,4-bis(diphenylphosphino) butane (DPPB), were considered. These ligands contain two phosphorus (P) atoms, each of which can coordinate to Pb²⁺ ions via its lone pair electrons, thereby passivating halide vacancies on the surface of CsPbI₃ QDs [37, 38]. The ligands differ in the number of carbon atoms connecting the P atoms (1, 2, 3, and 4 carbon atoms for DPPM, DPPE, DPPP, and DPPB, respectively), which leads to different P–P separation between them.

We performed density functional theory (DFT) calculations to evaluate whether each bidentate phosphine ligand has a suitable molecular configuration for surface passivation of CsPbI₃ QDs (Figure 1b). In the case of DPPM and DPPP, which have an odd number of carbon atoms between the two P atoms, their energy-minimized structures show that both P atoms are oriented in the same direction. This configuration allows them to simultaneously and effectively coordinate with two adjacent halide vacancies on the QD surface. The coordination of the P atoms to the QD surface is likely to be minimally hindered by the phenyl groups, as these groups are bent away from the direction the P atoms are facing. Indeed, previous studies have reported the effective binding of ligands containing bulky aromatic rings to QD surfaces [39]. In contrast, DPPE and DPPB, which contain an even number of carbon atoms between the P atoms, adopt energy-minimized structures in which the P atoms face opposite directions. Recent studies have shown that fine-tuning the orientational anchoring position of Lewis-base ligands—such as employing para-substituted thiol–pyridine (4-MP)—can significantly enhance the binding strength and surface coverage on CsPbI₃ QDs, thereby improving both electronic coupling and phase stability [23]. As a result, simultaneous coordination of both P atoms to the QD surface is expected to be significantly less effective in DPPE and DPPB due to steric hindrance from the phenyl groups. Therefore, DPPM and DPPP were selected as the bidentate phosphine ligands used for this study, and all subsequent discussions focus on these two ligands. Additional experimental verification of this structure–binding relationship is provided later in Section 2.3.

We hypothesize that the effectiveness of halide vacancy passivation through ligand exchange will differ between DPPM and DPPP. It is expected that for a bidentate ligand to coordinate efficiently, the distance between its two binding groups should closely match the distance between adjacent binding sites on the QD surface. The P–P separation in DPPP (~5.58 Å) is comparable to the lattice constant of CsPbI₃ (~6.20 Å for cubic α -phase CsPbI₃) [40], suggesting that the two P atoms in DPPP can effectively coordinate with adjacent I[−] vacancies in a lattice-matched configuration. In contrast, the shorter P–P separation in DPPM (~3.09 Å) is significantly smaller than the lattice constant of CsPbI₃, which may make simultaneous coordination of both P atoms less favorable and result in a lattice-mismatched configuration (Figure 1c).

The fabrication of the CsPbI₃ QD films and the subsequent postsynthetic ligand exchange process to replace surface ligands of QDs are schematically illustrated in Figure 1d. CsPbI₃ QDs were synthesized via a conventional hot-injection method employing OA and OAM as capping ligands. Successful synthesis of highly crystalline and monodisperse QDs was confirmed by transmission electron microscopy (TEM), which revealed the cubic shape of the QDs with an average particle size of ~10 nm (Figure S1). The synthesis of CsPbI₃ QDs was followed by purification using methyl acetate (MeOAc). This purification process not only removes impurities such as unreacted precursors but also promotes the ligand exchange of long-chain oleate (OA[−]) with shorter acetate (OAc[−]) ligands, as previously reported [41–43]. The purified CsPbI₃ QDs were redispersed in octane and deposited as thin films via spin coating. To perform ligand exchange with DPPM or DPPP, a solution of the respective ligand (i.e., DPPM or DPPP) dissolved in MeOAc was spin-coated onto the MeOAc-QD film, followed by rinsing with pure MeOAc. The resulting ligand-exchanged QD films are hereafter referred to as the “DPPM-QD” film and “DPPP-QD” film, respectively. As a control sample for comparison, films were also prepared by performing only a pure MeOAc washing step without the deposition of DPPM or DPPP solutions. The films will hereafter be referred to as the “MeOAc-QD” film. Further details on the synthesis and purification of CsPbI₃ QDs, as well as the procedures for QD film fabrication and ligand exchange, can be found in the Experimental section and the Supporting Information.

2.2 | Characterization of Ligand Exchange Using DPPM and DPPP

To compare the binding strength of DPPM and DPPP to halide vacancies on the CsPbI₃ surface, DFT calculations were performed (Figure 2a). The energy-minimized configuration was obtained for each ligand–CsPbI₃ complex, where either DPPM or DPPP was placed at two adjacent I[−] vacancy sites on a CsPbI₃ slab. Based on these optimized structures, the binding energy (E_b) of each ligand was calculated using the following equation,

$$E_b = E_{\text{PVK-L}} - E_{\text{PVK}} - E_L \quad (1)$$

where $E_{\text{PVK-L}}$ is the total energy of the energy-minimized CsPbI₃–ligand complex, E_{PVK} is the energy of the isolated CsPbI₃ slab, and E_L is the energy of the isolated ligand molecule. The calculated E_b s were −2.18 eV for DPPP and −1.42 eV for DPPM, confirming that DPPP binds more strongly to halide vacancies than DPPM when both phosphorus atoms coordinate to two directly adjacent I vacancies aligned along the (100) direction. To further clarify the preferred binding configuration of DPPP, we also compared two different vacancy geometries: direct (100) adjacent vacancies and diagonal (110) adjacent vacancies. Given that the P–P distance of DPPP is ~5.58 Å while the Pb–Pb distance across (110) diagonal vacancies is ~8.68 Å, we anticipated that such diagonal binding would be geometrically less favorable. Indeed, DFT calculations showed that the interaction energy for diagonal binding (−0.81 eV) is far less favorable than that for direct (100) adjacent binding (−2.19 eV), supporting the conclusion that coordination to two directly (100) adjacent I vacancies is energetically preferred (Figure S2).

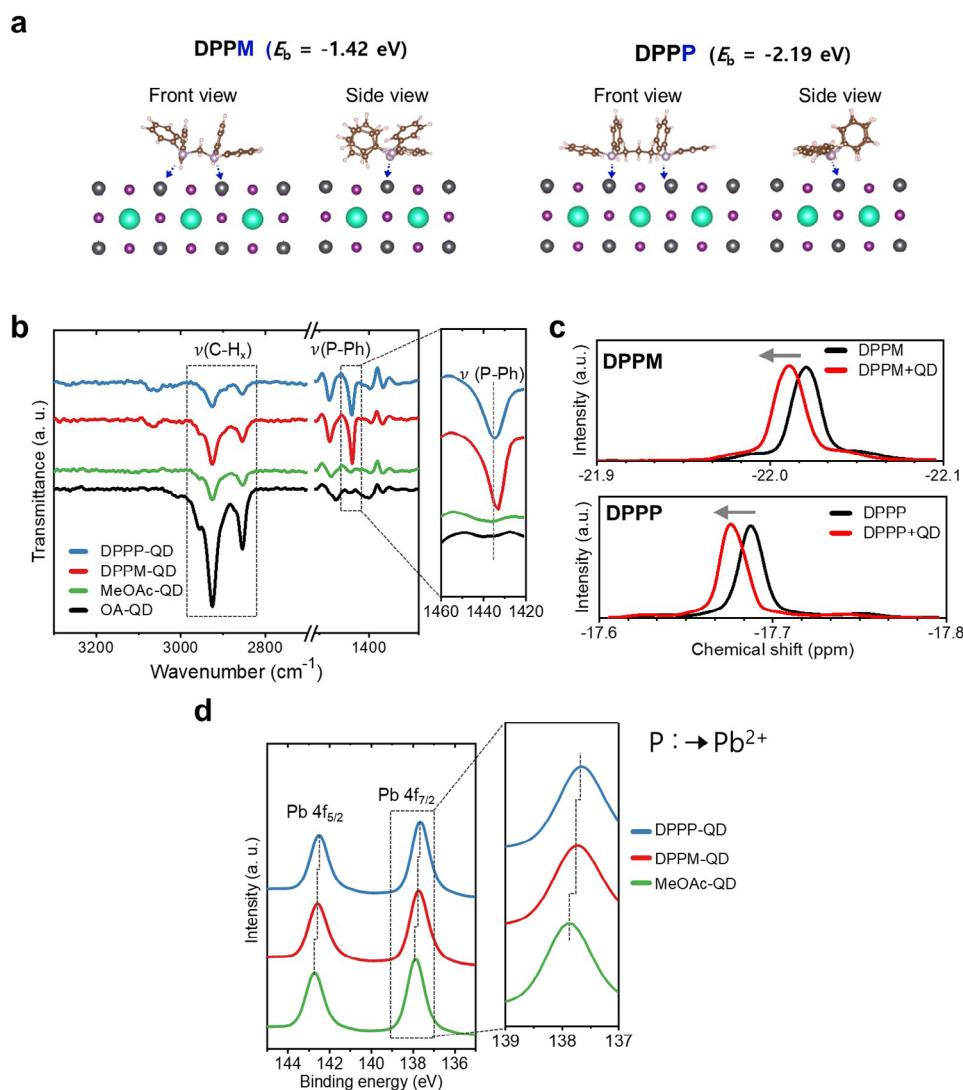


FIGURE 2 | Characterization of ligand exchange using DPPM and DPPP. (a) DFT-calculated binding energies and configurations of DPPM and DPPP on CsPbI₃ QD surfaces at adjacent halide vacancies. (b) FT-IR spectra of CsPbI₃ QD films confirming successful ligand exchange with the bidentate phosphine ligands. (c) ³¹P NMR spectra of DPPM and DPPP in the absence and presence of the CsPbI₃ QDs. (d) Pb 4f XPS spectra of CsPbI₃ QD films.

In addition, we considered the possibility that two DPPM molecules might each coordinate to two directly (100) adjacent I vacancies. Although the P–P distance of DPPM in its lowest-energy conformation (~ 3.09 Å) is roughly half of the CsPbI₃ lattice spacing (6.20 Å), the overall molecular dimension—measured as the distance between the outer ends of its phenyl rings—is much larger (~ 12.34 Å, Figure S3), and the four bulky phenyl rings impose substantial steric hindrance. Owing to these steric effects, the simultaneous accommodation of two DPPM molecules on adjacent vacancy sites is expected to be infrequent.

We further examined the possibility that a single DPPP molecule could simultaneously bridge two neighboring CsPbI₃ QDs. For such binding to occur, the molecule would have to reside in the narrow interparticle gap and adopt a highly twisted configuration in which its four phenyl groups do not hinder coordination of the two P atoms to I vacancies on separate QDs. However, DFT calculations in which the C–P torsion angle of DPPP was systematically rotated revealed that a 60° deviation

from the lowest-energy geometry raises the molecular energy by about 17 kJ mol⁻¹ (Figure S4). Such an energy barrier would strongly hinder the DPPP molecule from adopting a molecular configuration that enables binding to two different QDs. Therefore, we consider the possibility of a single DPPP molecule binding simultaneously to two different QDs to be practically negligible.

These combined results demonstrate that the spatial arrangement of the binding functional groups in bidentate ligands critically determines their binding stability on the CsPbI₃ QD surface vacancies. In particular, the distance between the two binding groups plays a decisive role in controlling the effectiveness of surface vacancy passivation in LHP QDs.

To confirm whether ligand exchange was successfully achieved in the CsPbI₃ QD films, Fourier transform infrared (FT-IR) spectroscopy was conducted (Figure 2b). The thicknesses of all films were carefully controlled to remain consistent. The peaks observed at 2957 cm⁻¹, 2925 cm⁻¹, and 2854 cm⁻¹ correspond to

vibrational modes of CH_2 groups ($\nu(\text{C-H}_x)$) [44, 45]. In the as-cast QD film (not washed by pure MeOAc), hereafter referred to as the “OA-QD” film, the intensities of these peaks were significantly higher than those of the other films; this is consistent with the dominant presence of long-chain ligands in the OA-QD film. In contrast, the MeOAc-film exhibited substantially reduced intensities of these peaks, suggesting that the native OA and OAm ligands were effectively replaced by shorter-chain MeOAc molecules. In both the DPPM-QD and DPPP-QD films, the peaks at 2957 cm^{-1} , 2925 cm^{-1} , and 2854 cm^{-1} were observed with intensities comparable to those in the MeOAc-QD film. In these samples, the peaks are partially attributable to CH_2 groups that connect the two P atoms in the DPPM and DPPP molecules. Notably, a distinct peak at 1435 cm^{-1} was present in the DPPM-QD and DPPP-QD films but was absent in the OA-QD and MeOAc-QD films. This peak originates from the vibration of the P-phenyl bond ($\nu(\text{P-Ph})$) of DPPM and DPPP [39, 46], and thus clearly supports the presence of DPPM and DPPP ligands in the DPPM-QD and DPPP-QD films, respectively.

The interaction between the P atoms of DPPM and DPPP and the CsPbI_3 QDs was confirmed by the ^{31}P nuclear magnetic resonance (NMR) spectra (Figure 2c). Compared to pure DPPM, the mixture of DPPM and CsPbI_3 QDs exhibited a downfield shift in the ^{31}P NMR peak. This shift indicates a decrease in the electron density at the P atoms due to coordination with Pb^{2+} ions in the QDs, resulting in deshielding of the P nuclei. A similar result was observed in the ^{31}P NMR spectrum of DPPP.

Furthermore, coordination of P atoms of DPPM and DPPP to Pb^{2+} (i.e., I^- vacancy passivation by DPPM and DPPP) was confirmed by using X-ray photoelectron spectroscopy (XPS) analysis (Figure 2d). In the Pb 4f XPS spectra of the samples, the Pb $4f_{5/2}$ and $4f_{7/2}$ peaks of the DPPM-QD and DPPP-QD films were shifted to lower binding energies compared to those of the MeOAc-QD film. This indicates that the Pb^{2+} ions in the CsPbI_3 QDs became relatively electron-rich due to coordination with the lone pair electrons of the P atoms in DPPM or DPPP through Lewis base interactions. The shift to lower binding energy was more pronounced in the DPPP-QD film than in the DPPM-QD film, suggesting that DPPP, with its lattice-matched molecular geometry, coordinates more effectively with Pb^{2+} ions than DPPM. At the same time, the Cs 3d and I 3d regions were recorded under identical conditions, and as shown in Figure S5, the Cs $3d_{3/2}$ and Cs $3d_{5/2}$ peaks and the I $3d_{5/2}$ and I $3d_{3/2}$ peaks remain essentially unchanged in both position and shape after ligand exchange. The absence of any measurable chemical-shift or line-shape variation demonstrates that the DPPM and DPPP ligands coordinate to Pb rather than to Cs or I atoms. These findings clearly indicate that the introduced bidentate ligands selectively coordinate with Pb^{2+} surface sites.

Overall, the Pb 4f XPS and ^{31}P NMR results provide strong evidence that the P atoms in both DPPM and DPPP effectively coordinate with Pb^{2+} ions on the QD surface, thereby passivating halide vacancies. This passivation is relatively more effective with the lattice-matched ligand DPPP than with the lattice-mismatched ligand DPPM.

2.3 | Trap Analysis of Ligand-Exchanged CsPbI_3 QD Films

To investigate the effects of introducing the bidentate phosphine ligands DPPM and DPPP on the trap passivation of CsPbI_3 QD films, as well as how the P-P separation within these ligands influences their effectiveness, we analyzed the trap states of ligand-exchanged CsPbI_3 QD films.

First, the PLQYs of the CsPbI_3 QD films were measured. Surface vacancy passivation by ligands reduces the density of trap states in the QDs, which in turn leads to a decrease in the population of non-radiative recombination centers; therefore, the more effectively a ligand passivates surface vacancies, the higher the PLQY of the QD [22]. The PLQY of each QD film was determined from its steady-state photoluminescence (PL) spectrum under excitation at 405 nm. The measured PL spectra are presented in Figure 3a, along with the corresponding UV-vis absorption spectra of each film. The calculated PLQYs were 7.9%, 13.5%, and 51.4% for MeOAc-QD film, DPPM-QD film, and DPPP-QD film, respectively (Figure 3b). The low PLQY of the MeOAc-QD film is consistent with previous reports. This has been attributed to the partial removal of surface I^- ions during treatment with MeOAc, due to its polarity, although it is relatively lower than that of other common polar solvents [43]. Ligand exchange with DPPM or DPPP resulted in increased PLQYs compared to the MeOAc-QD film, indicating more effective surface vacancy passivation by these ligands. In particular, the significantly higher PLQY observed for the DPPP-QD film compared to the DPPM-QD film suggests that DPPP enables more efficient passivation. This can be attributed to the molecular geometry of DPPP, which is more lattice-matched to the CsPbI_3 surface than that of DPPM. In addition, we examined CsPbI_3 QDs that were ligand-exchanged with DPPE and DPPB to clarify the influence of molecular geometry on passivation efficiency. As shown in Figure 1b, the minimum-energy structures of DPPE and DPPB adopt anti-staggered conformations in which the two phosphorus atoms face opposite directions, a geometry that hampers simultaneous coordination of both donor atoms to adjacent surface vacancies. Consistently, the PLQY of DPPE-QD and DPPB-QD films reached only 8.7% and 8.9%, respectively (Figure S6), which is higher than that of MeOAc-QD films but markedly lower than that of DPPM- and DPPP-treated films. These combined results indicate that the anti-staggered molecular geometry of DPPE and DPPB limits their surface binding strength and coverage, explaining their comparatively weaker passivation capability.

To further support the effectiveness of ligand-induced passivation, complementary surface analyses were conducted. As shown in Figure S7, the contact angle increased from 46.7° (MeOAc-QD) to 73.1° (DPPM-QD) and 74.3° (DPPP-QD), reflecting enhanced hydrophobicity due to the phenyl-functionalized ligands. In addition, PL mapping images (Figure S8) revealed increasing PL intensity and film uniformity from MeOAc-QD to DPPM-QD and DPPP-QD, indicating reduced trap-mediated quenching and improved spatial consistency in photoluminescence.

Differences in the degree of surface vacancy passivation among the CsPbI_3 QD films were also confirmed through surface

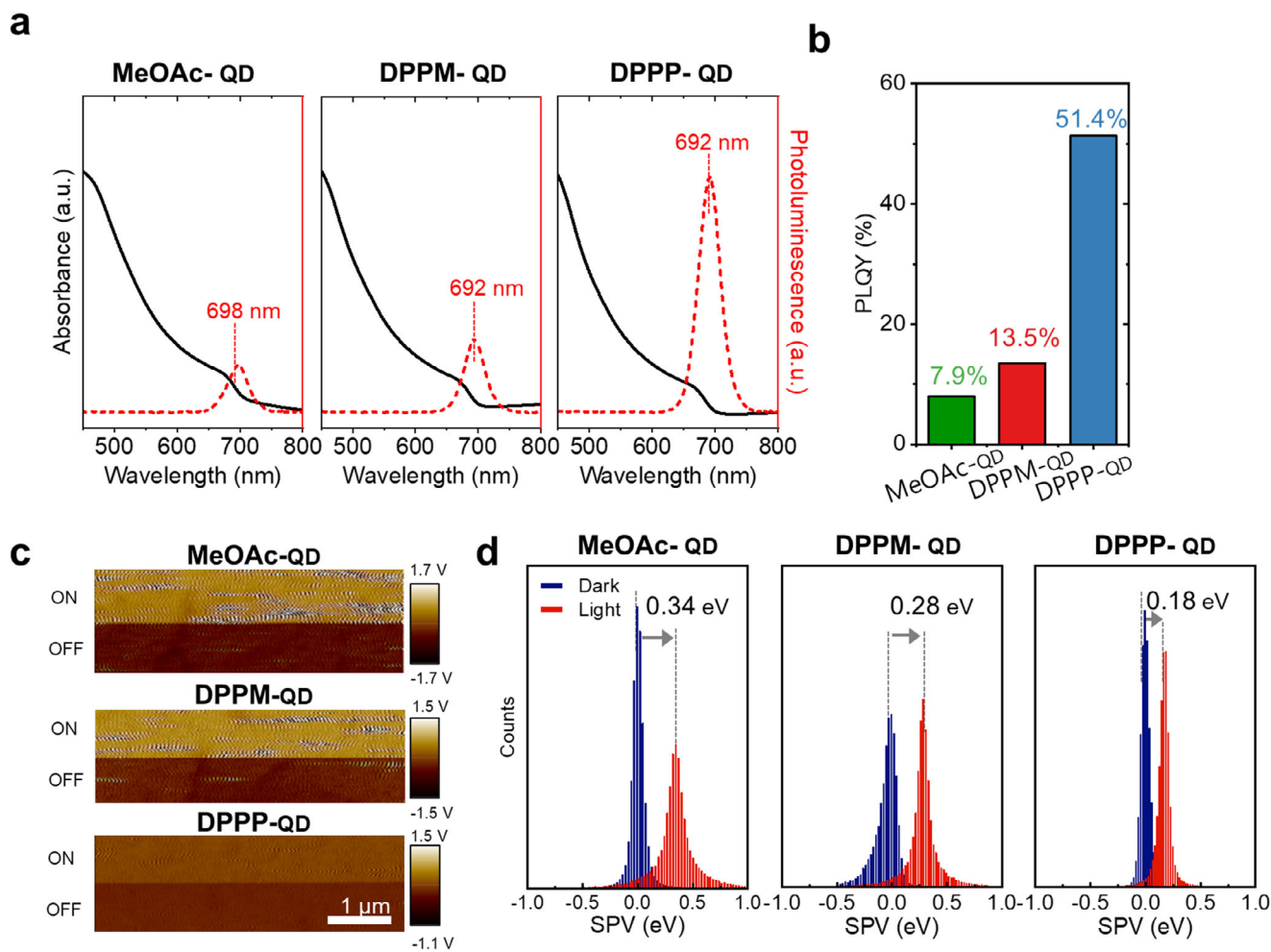


FIGURE 3 | Analysis of trap passivation in CsPbI₃ QD films with different ligands. (a) UV-vis absorption and PL spectra. (b) PLQY calculated from the PL spectra in (a). (c) KPFM images of the films in the dark and under illumination. Scale bar: 1 μ m. (d) SPV measurements derived from the KPFM images shown in (c).

photovoltage (SPV) measurements (Figure 3c,d). Here, SPV refers to the measurement of changes in surface potential induced by light illumination on the film. In general, films with surface traps exhibit band bending near the surface due to the accumulation of trapped charges, and the extent of this bending depends on the density of surface traps [47, 48]. Upon illumination, the band bending is reduced either by the detrapping of charges from trap states by photoexcitation or by the drift of photogenerated charge carriers driven by the surface built-in electric field. This change in band bending by light illumination is observed as a variation in surface potential before and after the illumination. Therefore, SPV measurements can provide information on both the dominant type of trap states on the film surface (i.e., whether electron or hole traps are more prevalent) and the density of the trap states. That is, the sign (positive or negative) of the SPV signal indicates the dominant trap type, while its magnitude reflects the density of the traps. For instance, in a film where electron trapping is predominant, an upward band bending occurs near the film surface, resulting in a positive SPV signal, and the magnitude of the SPV increases with increasing electron trap density. Further details on the principles underlying SPV measurements can be found in previous literature [47, 48].

We performed SPV measurements on the CsPbI₃ QD films by using Kelvin probe force microscopy (KPFM) to measure changes in the contact potential difference (CPD) of the films under light illumination and in the dark (Figure 3c,d). All samples exhibited positive SPV signals (which correspond to negative changes in CPDs), indicating that electron trapping is dominant in these films. We attribute this electron trapping to trap states near the CBM of CsPbI₃ QDs induced by I⁻ vacancies, as mentioned earlier in the Introduction section. The magnitude of the SPV was measured to be 0.34 eV for the MeOAc-QD film, 0.28 eV for the DPPM-QD film, and 0.18 eV for the DPPP-QD film. These values indicate that the electron trap density is lowest in the DPPP-QD film, followed by the DPPM-QD and then the MeOAc-QD film. This trend is in excellent agreement with the PLQY measurements, further confirming that halide vacancies are most effectively passivated in the order of DPPP-QD, DPPM-QD, and MeOAc-QD films.

Furthermore, the improved defect passivation led to greatly enhanced long-term optical stability under ambient storage conditions (25°C, 20–30% RH). Figure S9 shows that MeOAc-QD films began to exhibit a shoulder peak around 415 nm within just one day, a signature of the cubic-to- δ phase transformation

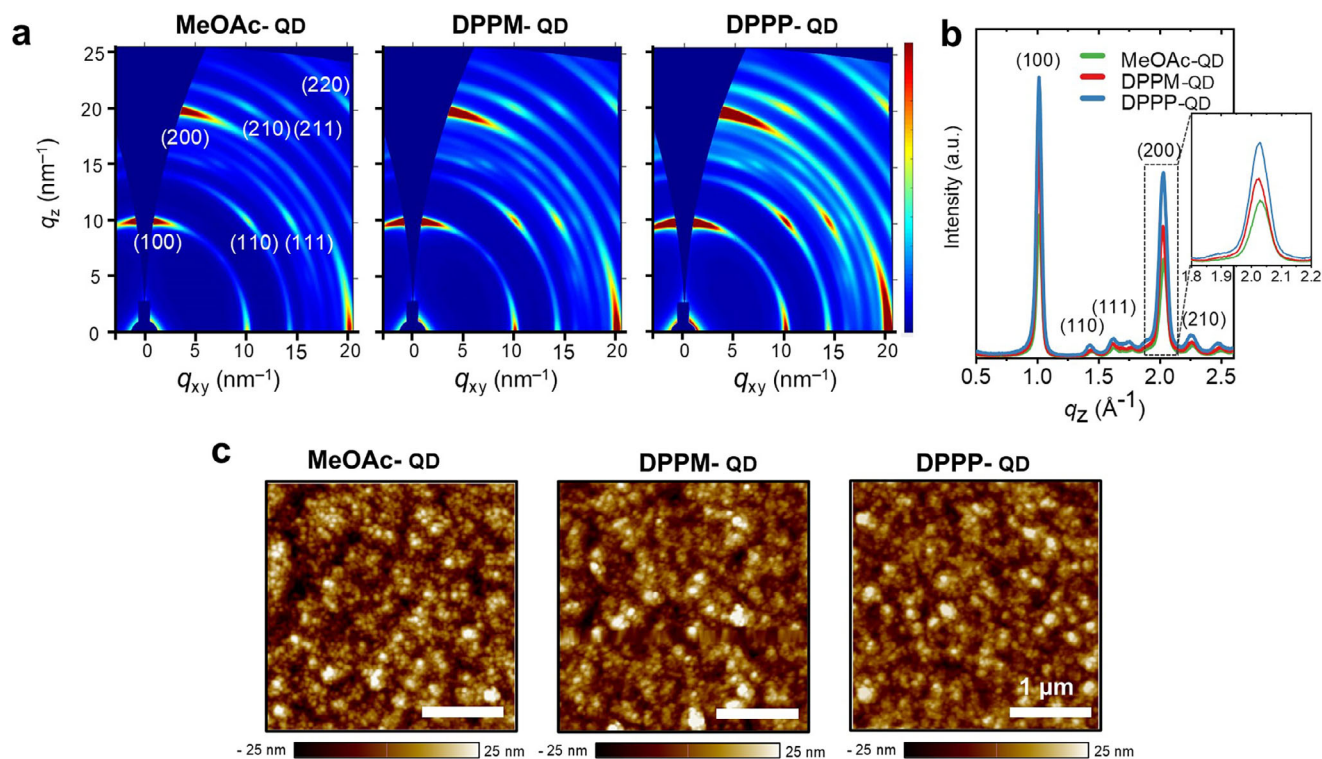


FIGURE 4 | Microstructural analysis of CsPbI₃ QD films. (a) 2D GIXD patterns of CsPbI₃ QD films with different ligands. (b) 1D out-of-plane line-cut profiles extracted from the GIXD patterns in (a). (c) AFM height images of the CsPbI₃ QD films.

[23], and were almost completely converted to the δ -phase after 135 days. This rapid degradation is attributed to partial removal of surface I⁻ ions during MeOAc treatment, which creates polar vacancy sites that facilitate oxygen and moisture ingress [49]. DPPM-QD maintained its perovskite absorption features for about 10 days but displayed a similar shoulder peak after 135 days, indicating partial phase transition. By contrast, DPPP-QD retained nearly unchanged absorption spectra even after ~135 days of storage, clearly demonstrating that ligand exchange with DPPP significantly suppresses the formation of the δ -phase and thereby provides superior long-term phase stability.

Consistent with these absorption results, the PL stability of the QD films was also evaluated under the same ambient conditions (25°C, 20–30% RH) for approximately 18 days (Figure S10). The PL intensity of the MeOAc-QD dropped to near-complete degradation within about 8 days, whereas the DPPM-QD retained 47.4% and the DPPP-QD retained 89.2% of their initial PL intensity even after 18 days of storage. These PL data corroborate the UV-vis findings, further confirming that DPPP provides the most effective long-term suppression of phase degradation among the tested ligands.

The PLQY and SPV results collectively confirm that ligand exchange with DPPM or DPPP leads to effective trap passivation of CsPbI₃ QDs. Moreover, the findings demonstrate that trap passivation is significantly more efficient with DPPP, which adopts a lattice-matched geometry, compared to DPPM, which exhibits a lattice-mismatched geometry. These results allow us to conclude that controlling the distance between the two binding

functional groups in a bidentate ligand is a critical parameter for effective surface trap passivation in LHP QDs.

2.4 | Effect of Ligand Exchange on Film Microstructure

To investigate the effect of ligand exchange from MeOAc to DPPM or DPPP on the microstructure of CsPbI₃ QD films, 2D grazing-incidence X-ray diffraction (GIXD) measurements were conducted on the corresponding films (Figure 4a,b). All films exhibited well-defined (100), (110), (111), (200), (210), (211), and (220) diffraction peaks, and the peak positions matched well with those previously reported for cubic-phase CsPbI₃ QD films [25, 26, 50]. The essentially unchanged peak positions across different ligands confirm that the perovskite crystal structure remains intact during ligand exchange. Quantitative peak fitting of the (100) and (200) reflections (Table S1) further revealed that the full widths at half maximum (FWHM) are nearly identical among the three samples, indicating that the ligand treatments do not measurably alter the crystallite size or coherence length of the QDs [28, 29].

Notably, the diffraction intensities increased in the order MeOAc-QD < DPPM-QD < DPPP-QD, with the out-of-plane (100) peak of the DPPP-QD film being roughly twice as intense as that of the MeOAc-QD film. All three films were prepared to have the same thickness, so the intensity difference cannot be ascribed to variations in film thickness. Considering that the FWHM remains essentially unchanged, the higher intensity is more plausibly related to a greater amount of diffracting material per unit volume

rather than to an increase in the crystallinity of individual QDs. Previous studies have suggested that effective surface passivation can facilitate more complete ligand exchange and thereby reduce residual OA/OAm with long alkyl chains [22]. This reported mechanism provides a reasonable context for understanding the observed intensity enhancement while remaining consistent with literature showing that ligand exchange typically alters only the surface chemistry without significantly changing the crystal lattice of CsPbI₃ QDs.

To gain further insight into the microstructure of the CsPbI₃ QD films, we examined their surface morphology by atomic force microscopy (AFM) (Figure 4c). For each sample (MeOAc-QD, DPPM-QD, and DPPP-QD), five different regions were scanned (Figure S11), and the average root-mean-square (RMS) roughness values with standard deviations calculated from these scans are presented in Figure S12. The AFM measurements reveal a modest decrease in RMS roughness after ligand exchange, suggesting slightly smoother surfaces. These combined observations indicate that ligand exchange with DPPM or DPPP contributes to mildly improved surface smoothness and film uniformity while preserving the overall structural integrity of the CsPbI₃ QD films.

2.5 | Performance of Photodetectors Based on Ligand-Exchanged CsPbI₃ QDs

To investigate the impact of ligand exchange with DPPM or DPPP on the performance of CsPbI₃ QD-based optoelectronic devices, photodiodes were fabricated using MeOAc-QD, DPPM-QD, and DPPP-QD films, and their characteristics were compared. The device architecture of the fabricated devices is illustrated in Figure 5a. Fluorine-doped tin oxide (FTO) was used as the transparent electrode, with a TiO₂ layer deposited as the electron transport layer. On top of the CsPbI₃ QD photoactive layer, 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) and MoO_x were employed as the hole transport layer, followed by a silver (Ag) layer as the top electrode. Details of the device fabrication process are provided in the Experimental section.

All devices exhibited a broad photoresponse across the entire visible spectrum, ranging from 300 nm to 700 nm. The peak responsivity followed the order of MeOAc-QD, DPPM-QD, and DPPP-QD devices, as shown in Figure 5b. The DPPP-QD-based device achieved the highest responsivity of 0.376 A W⁻¹ at 550 nm. The current density–voltage (*J*–*V*) characteristics of each device in the dark are shown in Figure 5c. The results indicate that ligand exchange with bidentate phosphine ligands effectively suppresses the dark current compared to the MeOAc-QD device; for example, at a bias of –2 V, the dark current densities were measured to be 6.55 × 10⁻³ mA cm⁻², 4.53 × 10⁻³ mA cm⁻², and 3.38 × 10⁻³ mA cm⁻² for MeOAc-QD device, DPPM-QD device, and DPPP-QD device, respectively. In addition, the noise current density spectra as a function of modulation frequency revealed that the DPPP-QD-based device also exhibited the lowest noise level, followed by the DPPM-QD device, and then the MeOAc-QD device (Figure 5d). The lower dark current observed in the DPPM-QD and DPPP-QD devices relative to the MeOAc-QD device is likely to contribute

to this trend [30]. To further confirm proper device operation, we additionally measured continuous light-switching photocurrents under 525 nm illumination (1.73 μW cm⁻²). As shown in Figure S13, all devices exhibited stable and reproducible on/off photocurrent responses over ~300 s without noticeable signal degradation, and the photocurrent amplitude agreed well with the responsivity values determined from Figure 5b. This measurement confirms the reliable and consistent photoresponse of the DPPM- and DPPP-QD photodetectors under repeated light on/off cycling.

Owing to the synergistic effect of high responsivity and low noise current, the DPPP-QD-based device demonstrated the highest specific detectivity (*D*^{*}) among all devices (Figure 5e). The *D*^{*} value reached 5.67 × 10¹² Jones at 550 nm (measured at zero bias with a light modulation frequency of 45 Hz), which is comparable to that of commercial silicon photodiodes. This value is more than three times higher than that of the DPPM-QD device (*D*^{*} = 1.82 × 10¹² Jones) and nearly one order of magnitude (~9 times) higher than that of the MeOAc-QD device (*D*^{*} = 6.31 × 10¹¹ Jones). Note that the *D*^{*} was calculated using the following equation,

$$D^* = \frac{R\sqrt{A}}{i_N} \quad (2)$$

where *R* is the responsivity, *A* is the device area (0.0555 cm²), and *i_N* is the noise current. To avoid overestimation of *D*^{*}, the value of *i_N* was taken directly from the noise current spectrum shown in Figure 5d, at the same light modulation frequency used for the responsivity measurement (45 Hz). The numerical values of *R*, *A*, and *i_N* used in the *D*^{*} calculation are summarized in Table S2. To the best of our knowledge, the *D*^{*} value of 5.67 × 10¹² Jones achieved by the DPPP-QD-based photodiode is among the highest values reported for LHP QD-based photodiodes to date. Table 1 summarizes *D*^{*}s of representative LHP QD-based photodiodes previously reported in the literature [51–57]. Some of the reported values were estimated using an approximate equation that relies on dark current for calculating *D*^{*}, a method that is generally known to result in overestimation [58]. In contrast, the *D*^{*} values in this study were calculated using directly measured noise current, a method that minimizes overestimation and yields more reliable values. Considering this, we believe that the performance of the DPPP-QD-based photodiode demonstrated in this work would rank among the best reported.

As an additional method to demonstrate the photoresponse of our photodetectors, we measured the photocurrent of our devices under progressively attenuated light intensity to evaluate their ability to detect weak light signals. In other words, we directly measured the noise equivalent power (NEP) of our photodetectors (Figure S14). Specifically, we modulated a 525 nm light source at 45 Hz and gradually reduced the incident light power from 0.64 pW Hz^{-0.5} until the photoresponse became indistinguishable from the noise current. The results revealed that the NEP was lowest for the DPPP-QD-based device (0.15 pW Hz^{-0.5}), followed by the DPPM-QD (0.19 pW Hz^{-0.5}) and MeOAc-QD (0.23 pW Hz^{-0.5}) devices, which is consistent with the trend of *D*^{*}.

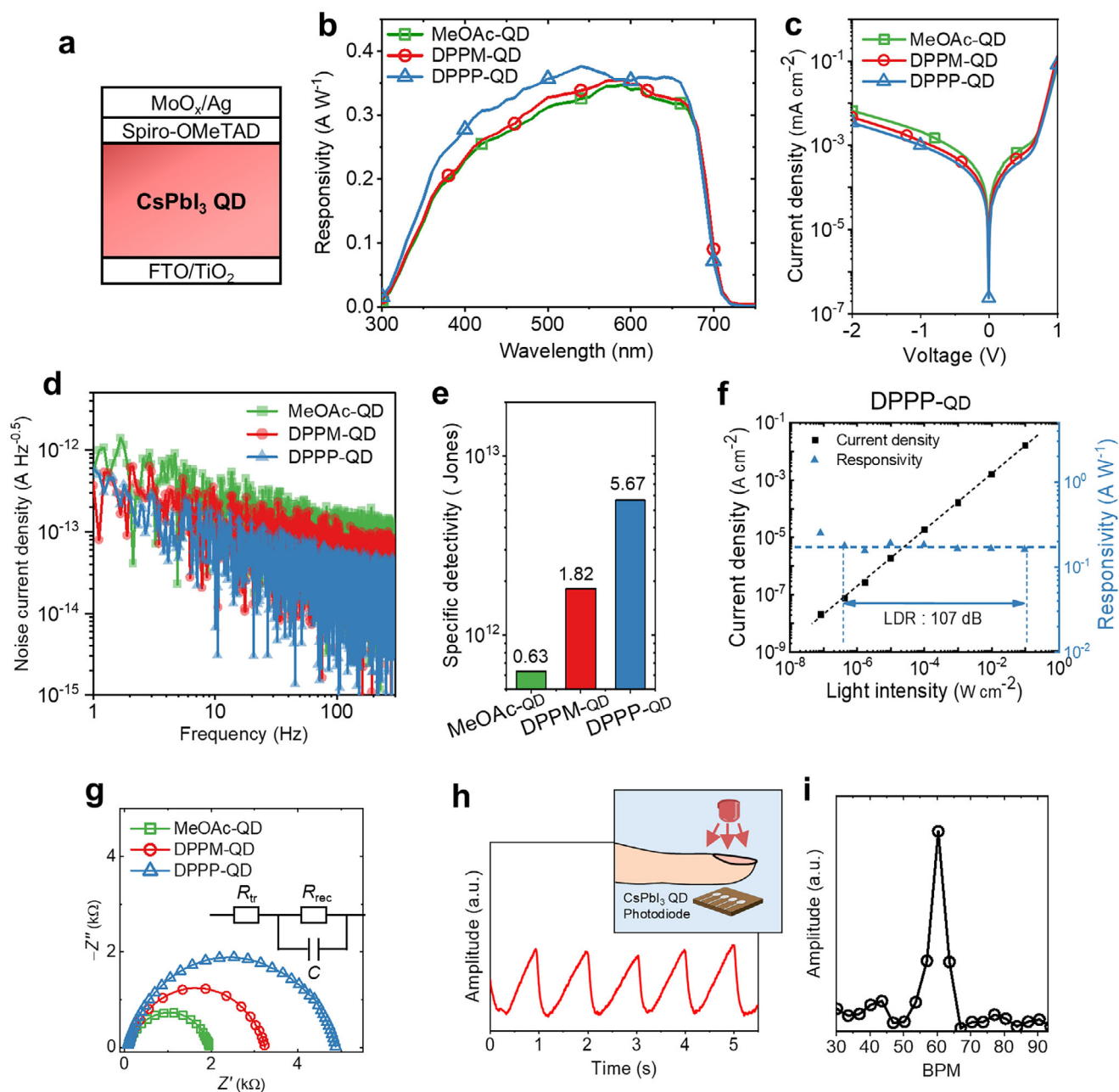


FIGURE 5 | Characteristics of photodiodes based on CsPbI₃ QDs. (a) Schematic illustration of the device structure. (b) Responsivity spectra of the photodiodes. (c) Current density–voltage (J – V) characteristics measured in the dark. (d) Noise current density as a function of frequency. (e) Specific detectivity of the devices under 550 nm illumination, calculated from the responsivity and noise current measured at 45 Hz. (f) Light-intensity dependence of the photocurrent and responsivity of the DPPP-QD photodiode measured at 0 V bias. The linear dynamic range (LDR) of the device was determined to be ~ 107 dB. (g) Nyquist plots of device data obtained from electrochemical impedance spectroscopy. The inset shows the equivalent circuit model used for curve fitting. (h) Time-domain PPG signal recorded using the DPPP-QD-based photodiode. The inset shows the schematic of a PPG sensor application. (i) Frequency-domain representation of the PPG signal obtained by Fourier transforming the data shown in (h), demonstrating accurate detection of heart rate (~ 60 bpm).

To further characterize the light-intensity-dependent photore-sponse of the devices, we measured the J – V characteristics of our photodetectors under various illumination intensities (Figure S15). The illumination intensity was varied in the range of 10^{-7} – 10^{-1} W cm $^{-2}$ using a solar simulator and neutral density filters, and only representative J – V curves are shown in Figure S15 for clarity of presentation. It is clearly observed that the photocurrent increases progressively with increasing illumination

intensity for all devices. Notably, at all illumination intensities, the magnitude of the photocurrent follows the order DPPP-QD device > DPPM-QD device > MeOAc-QD device, consistent with the trend shown earlier. For the DPPP-QD photodiode, we evaluated the linear dynamic range (LDR), which quantitatively represents the range of light intensities over which the photode-tector generates a photocurrent that is linearly proportional to the incident light intensity. The LDR was calculated according to

TABLE 1 | Specific detectivities of representative LHP QD-based photodiodes previously reported in the literature.

Device structure	Responsivity, R (A W ⁻¹)	Noise current, i_N (A Hz ^{-0.5})	Specific detectivity, D^* (Jones)	Reference
FTO/TiO ₂ /CsPbI ₃ QDs/Spiro/MoO _x /Ag	0.376	1.56×10^{-14}	5.67×10^{12} (550 nm, 0 V)	This work
ITO/ZnO/CsPbI ₃ QDs/P3HT/MoO ₃ /Ag	0.035	2.0×10^{-14} ^a	1.8×10^{12} (640 nm, -0.5 V)	[51]
FTO/TiO ₂ /CsPbI ₃ QDs/Spiro/Ag	0.105	N/A ^b	5.0×10^{13} (450 nm, 0 V) 3.0×10^{13} (700 nm, 0 V)	[52]
ITO/SnO ₂ /CsPbI ₃ QDs/Au	0.100	1.5×10^{-11}	1.0×10^{12} (500nm, 0 V)	[53]
ITO/PET/TiO ₂ /CsPbBr ₃ QDs/Spiro/Ni/Au	10.1	5.66×10^{-15} ^a	9.35×10^{13} (405 nm, 0 V)	[54]
FTO/TiO ₂ /MAPbI ₃ QDs/PTAA/MoO ₃ /Ag	0.30	1.0×10^{-13}	2.0×10^{11} (700 nm, 0 V)	[55]
ITO/SnO ₂ /CsPbBr ₃ NWs/PTAA/Au	0.30	3.92×10^{-14} ^a	1.0×10^{13} (473 nm, 0 V)	[56]
ITO/ZnO NRs/CsPbBr ₃ QDs/Spiro/Ag	0.14	N/A ^b	7.0×10^{11} (450 nm, -1V)	[57]

^aNoise current estimated from dark current; and^bNoise current not reported.

the equation, $LDR [dB] = 20 \log (P_{MAX}/P_{MIN})$, where P_{MAX} and P_{MIN} denote the maximum and minimum light intensities within the range in which the device exhibits a constant responsivity. As shown in Figure 5f, the DPPP-QD device maintained a constant responsivity over the illumination range of 4.5×10^{-7} to 0.1 W cm^{-2} , corresponding to an LDR of 107 dB.

We attribute the enhanced responsivity and reduced dark current of the photodiodes after ligand exchange with DPPM or DPPP to effective trap passivation. Trap states in LHP QDs act as quenching sites for excitons as well as recombination sites for separated free charge carriers, both of which lead to photocurrent loss [31]. Therefore, trap passivation induced by DPPM or DPPP, as discussed in detail in Section 2.3, leads to reduced photocurrent loss and consequently increased responsivity. This interpretation is further supported by the electrochemical impedance spectroscopy (EIS) analysis of the devices (Figure 5g). The Nyquist plots obtained from the measurements were well fitted using a simplified equivalent circuit model shown in the inset, where R_{tr} is the charge transport resistance, R_{rec} is the recombination resistance, and C_{bulk} is the bulk capacitance associated with the electrical charges within the device [32, 33, 59]. According to the fitting results, the values of R_{tr} were 109.7 Ω , 97.2 Ω , and 84.1 Ω for the MeOAc-QD device, DPPM-QD device, and DPPP-QD device, respectively, while the values of R_{rec} were 1843 Ω , 3143 Ω , and 4784 Ω for the MeOAc-QD device, DPPM-QD device, and DPPP-QD device, respectively. These results indicate progressively more efficient charge transport and reduced charge recombination in the order of MeOAc-QD, DPPM-QD, and DPPP-QD devices, likely due to increasingly effective trap passivation. It is also well established that a high surface trap density of QDs contributes to increased dark current of the QD-based photodiodes or photovoltaics [34, 60, 61]. Thus, it is reasonable to interpret the reduced dark current and noise current observed with DPPM and DPPP as a result of efficient trap passivation. Overall, the fact that DPPP provides more effective trap passivation than DPPM, leading to greater enhancements in responsivity and reductions in dark current, underscores the importance of matching the ligand's molecular geometry with the QD lattice (i.e., achieving lattice matching between the ligand and the QD) to optimize the performance of QD-based photodiodes.

Finally, we demonstrate the practical application of the fabricated CsPbI₃ QD-based photodiode in photoplethysmography (PPG) sensing (Figure 5h,i). A finger was placed on top of the DPPP-QD-based photodiode while a red LED was continuously illuminated, and the resulting photocurrent signal was recorded (Figure 5h, inset). The device successfully captured periodic pulsatile signals (Figure 5h), and by applying a Fourier transform to the time-domain data, the heart rate was determined to be ~60 beats per minute (Figure 5i). This result confirms that the lattice-matched ligand-engineered LHP QD photodiode developed in this study possesses sufficient performance for practical biomedical applications.

3 | Conclusion

In this study, we performed ligand exchange on CsPbI₃ QD films using bidentate phosphine ligands and systematically investigated how the intramolecular distance between the two coordinating functional groups of a bidentate ligand affects the passivation of surface halide vacancies and resulting trap states in QDs. DPPM and DPPP used in this study are both bidentate ligands containing two P atoms, which coordinate to I⁻ vacancies on the surface of CsPbI₃ QDs and thereby passivate the surface. The structural difference between the two lies in the number of carbon atoms connecting the two P atoms, which is one in DPPM and three in DPPP. This structural variation leads to differences in their ability to passivate vacancies. DPPP, with a P-P distance similar to the lattice spacing of CsPbI₃, showed stronger binding to surface halide vacancies and more effective passivation than DPPM, whose shorter P-P distance results in a geometry that does not match the CsPbI₃ lattice well. As a result, QD films treated with DPPP exhibited higher PLQY and lower surface trap density than those treated with DPPM. In addition, DPPP-QD films had smoother surface morphology and more ordered QD packing compared to DPPM-QD films. Photodiodes fabricated using these QD films showed notable differences in performance. Devices based on DPPP-QD films, having more effectively passivated surface vacancies and traps, exhibited higher responsivity along with lower dark current and noise current compared to those based on DPPM-QD films. Consequently, the DPPP-QD

photodiode achieved a specific detectivity three times higher than that of the DPPM-QD device and approximately ten times higher than that of the control device with MeOAc ligand. These findings demonstrate a new approach for developing high-performance LHP QD-based optoelectronic devices by controlling the molecular geometry of ligands, clearly showing that achieving geometric compatibility between the ligand structure and the QD lattice plays a critical role in determining the effectiveness of surface passivation of QDs and overall device performance.

4 | Experimental Section

4.1 | Materials

Oleic acid (OA, 90%) was purchased from Alfa Aesar. Cesium carbonate (Cs_2CO_3 , 99.995%, metals basis), 1-octadecene (ODE, 90%), oleylamine (OAm, 70%), octane (anhydrous, >99%), hexane (anhydrous, 95%), and methyl acetate (MeOAc, anhydrous, 99.5%) were obtained from Sigma-Aldrich. Diphosphine ligands, including bis(diphenylphosphino)methane (DPPM, 97%) and 1,3-bis(diphenylphosphino)propane (DPPP, 97%), were also sourced from Sigma-Aldrich, along with phenethylammonium iodide (PEAI), 4-tert-butylpyridine, and bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI). Titanium dioxide (TiO_2) precursor solution (0.15 M) and TiCl_4 aqueous solution (2 M) were purchased from Sharechem. Spiro-OMeTAD (LT-S922) was acquired from Lumtec.

4.2 | Device Fabrication

Patterned FTO-coated glass substrates (AMG Korea) were sequentially cleaned by sonication in detergent, deionized water, acetone, and isopropanol for 10 min each. The compact TiO_2 (c- TiO_2) electron-transport layer was deposited by spin-coating a precursor solution at 3000 rpm for 30 s, followed by annealing at 500°C for 1 h. After cooling to room temperature, the substrates were immersed in 120 mM TiCl_4 aqueous solution at 70°C for 1 h, rinsed with deionized water, and annealed again at 500°C for 1 h. To prepare the CsPbI_3 QDs layer, CsPbI_3 QD solution was spin-coated on the FTO/c- TiO_2 substrates in two steps: 20 s at 1000 rpm, followed by 20 s at 2000 rpm. Ligand exchange was performed using MeOAc solutions of DPPM or DPPP (0.25 mg mL⁻¹), applied to the film for 5 s, followed by rinsing with neat MeOAc. This process was repeated 4–6 times to achieve the desired film thickness of approximately 400 nm. The ligand-exchanged CsPbI_3 QD films were subsequently treated with PEAi (1 mg mL⁻¹ in ethyl acetate) for 5 s and rinsed with MeOAc. For the hole-transporting layer, 72.3 mg of spiro-OMeTAD was dissolved in 1 mL chlorobenzene with additives: 29 μL of 4-tert-butylpyridine and 17.5 μL of Li-TFSI solution (520 mg mL⁻¹ in acetonitrile). The resulting solution was spin-coated onto the CsPbI_3 QD layer at 4000 rpm for 30 s. Finally, MoO_x (10 nm) and Ag (100 nm) electrodes were sequentially deposited by thermal evaporation under high vacuum conditions with a base pressure maintained below 1×10^{-6} Torr. All spin-coating processes were carried out in a controlled-humidity dry box environment (relative humidity ~25%, room temperature).

4.3 | Film Preparation and Ligand Exchange

CsPbI_3 QDs dispersed in octane (75 mg mL⁻¹) were spin-coated onto substrates using a two-step procedure: 20 s at 1000 rpm followed by 20 s at 2000 rpm. Ligand exchange was conducted by spin-casting a 0.25 mg mL⁻¹ MeOAc solution of DPPM or DPPP onto the as-cast CsPbI_3 QD films for 5 s, followed by a rinsing step with pure MeOAc to remove unbound ligands.

4.4 | Solution-State ³¹P NMR Sample Preparation

DPPM-QD and DPPP-QD films were carefully scraped from the substrates and dissolved in deuterated toluene (D_8 -toluene) for solution-state ³¹P nuclear magnetic resonance (NMR) spectroscopy. The resulting solutions were transferred into NMR tubes and analyzed using a Bruker Avance 400 MHz spectrometer.

4.5 | Characterization

Current density–voltage (J – V) measurements were carried out using a Keithley 4200 source meter under dark conditions. A mask with an area of 0.0555 cm² was used for the electrode deposition. Responsivity was evaluated via photomodulation spectroscopy using a monochromatic light source modulated at 45 Hz. The optical setup consisted of a 500 W Hg(Xe) arc lamp, a grating monochromator ($\lambda = 254$ –2000 nm), and an optical chopper. The photocurrent was recorded using a Stanford Research Systems SR570 low-noise current preamplifier connected to an SR830 lock-in amplifier. Noise current was measured using a Zurich Instruments MFIA impedance analyzer in combination with SR830 lock-in amplification. For the PPG sensor application, a 640 nm LED was employed as the light source. The optical power was measured to be 2.19 $\mu\text{WHz}^{-0.5}$, and the intensity was calibrated using a reference photodiode (PVM 132, calibrated by NREL). This study involved non-invasive PPG measurements performed by one of the authors on themselves only. No personal identifiers or health-related data were collected. According to the regulations of the POSTECH Institutional Review Board, this activity does not constitute human subject research and is exempt from ethics review. Informed consent was obtained from the participant prior to the PPG measurements. Continuous light-switching photocurrent measurements were carried out under 525 nm LED illumination with an intensity of 1.73 $\mu\text{W cm}^{-2}$. The devices were subjected to periodic on/off light modulation at a frequency of 0.1 Hz, and the photocurrent was recorded continuously for 300 s to evaluate the stability and reproducibility of the photoresponse. Noise current and noise-equivalent power (NEP) were measured using a Zurich Instruments MFIA impedance analyzer in combination with SR830 lock-in amplification. A 525 nm LED modulated at 45 Hz was used as the light source, and its intensity was calibrated using a reference photodiode (PVM 132, calibrated by NREL). Electrochemical impedance spectroscopy (EIS) measurements were performed in the dark at zero bias using the MFIA system. Fourier transform infrared (FT-IR) spectra were recorded under vacuum using a Bruker VERTEX 70 spectrometer. Photoluminescence quantum yield (PLQY) was measured using a Hamamatsu Quantaaurus-QY (C11347-11) system with excitation at 405 nm.

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific ESCALAB 250Xi system. Grazing incidence wide-angle X-ray scattering (GIXD) was performed at the 3C and 9A beamlines of the Pohang Accelerator Laboratory (PAL), Korea. Surface morphology was investigated via atomic force microscopy (AFM, Digital Instruments Multimode). Photoluminescence (PL) mapping was conducted using Raman imaging mode on a Witec Alpha300R system equipped with a 532 nm excitation laser.

4.6 | Computational Methods

Geometry optimizations for the free DPPM, DPPE, and DPPP molecules were performed at the B3LYP/6-31G+(d,p) level of theory using the Gaussian 16 software package. To study the interactions between ligands and perovskite surfaces, DFT calculations were further conducted using the CASTEP module in Materials Studio 2020. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional within the generalized gradient approximation (GGA) framework was employed. Ultrasoft pseudopotentials were used to represent core electrons. All geometries were optimized with a 20 Å vacuum slab to avoid interaction between periodic slabs. The calculations used an energy cutoff of 630 eV and a $1 \times 1 \times 1$ k-point mesh, with convergence criteria of 1×10^{-5} eV per atom in energy, 0.03 eV Å^{-1} in force, and 0.001 Å in displacement.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: sml172211-sup-0001-SuppMat.docx.