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Pb²⁺-Doping-Activated Localized Luminescence of Organic-Inorganic Cobalt (II) Bromides

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Abstract

Transition-metal Co²⁺ ions in halide systems are generally regarded as inefficient emitters due to rapid nonradiative relaxation of their d-d excited states. Here, we prepared two zero-dimensional (0D) organic-inorganic hybrid cobalt halides, benzyl triphenyl phosphonium bromide cobalt ((BTP)₂CoBr₄) and triphenyl phosphonium bromide cobalt ((PPh₃)₂CoBr₄), composed of [CoBr₄]²⁻ tetrahedra embedded in distinct organic frameworks. Upon Pb²⁺ incorporation, both compounds exhibit visible photoluminescence composed mainly of two emission bands centered at approximately 450 and 500 nm, with decay lifetimes on the nanosecond timescale. The emission at 450 nm originates from d-d transitions associated with short-range Co-Co ferromagnetic (FM) interactions, whereas the 500 nm emission can be attributed to donor-acceptor pair (DAP) transitions involving Co and Pb. At low temperatures, an additional broadband emission centered at ~620 nm emerges in Pb²⁺-doped (PPh₃)₂CoBr₄, with lifetimes reaching the microsecond scale, while such emission is not observed in (BTP)₂CoBr₄. Low-temperature lattice contraction in the PPh₃ framework further shortens the Co-Co distance, thereby enhancing short-range FM interactions and leading to the formation of a magnetic bipolaron for emission. Overall, this work reveals the role of organic ligand structure and dopant modulation in regulating the Co-centered excited states, providing deeper insight into the interactions between cobalt ions and organic ligands in low-dimensional halide systems.

Keywords: cobalt halides; Pb²⁺ modulation; DAP; magnetic bipolaron

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1. Introduction

Organic-inorganic hybrid metal halides have attracted considerable interest in recent years owing to their highly designable crystal structures, tunable electronic properties, and diverse luminescence behaviors, showing great promise in solid-state lighting, displays, information encryption, and radiation detection [1–3]. In particular, 0D and low-dimensional metal halide systems composed of isolated inorganic polyhedra, such as [MX₄]²⁻ and [MX₆]²⁻ units, are characterized by pronounced excitation localization and strong electron-phonon coupling. These features render their excited states highly

sensitive to local structural environments, often giving rise to broadband emission, large Stokes shifts, and rich temperature-dependent photophysical responses [4–8]. Consequently, subtle modifications in lattice geometry, local distortion, and structural confinement can profoundly reshape the excited-state energy landscape in such materials. To date, most investigations of luminescent 0D hybrid halides have focused on clusters centered on main-group metal ions with an ns^2 electronic configuration (e.g., Pb^{2+} , Sn^{2+} , and Bi^{3+}) or d^{10} metal ions (e.g., In^{3+} , Zn^{2+} , and Cd^{2+}) [9–11]. In these systems, the interplay between the stereochemical activity of lone-pair electrons, local lattice distortion, and organic-inorganic dielectric contrast enables efficient localization of excited states and effective regulation of emission wavelength, bandwidth, and lifetime. By comparison, transition-metal ions introduce additional complexity owing to their open d-shell configurations, multiple spin states, and strong coupling to lattice vibrations, offering both challenges and opportunities for constructing unconventional luminescent centers [12,13].

However, luminescence from high-spin Co^{2+} (d^7) in conventional host lattices is typically subject to severe quenching by nonradiative d-d relaxation and is therefore widely regarded as intrinsically difficult to activate [14]. In conventional oxide and silicate matrices, such as $K_2ZnP_2O_7:Co^{2+}$ [15], $Mg_2SnO_4:Co^{2+}$ [16], and $Zn_2SiO_4:Co^{2+}$ microcrystalline glass [17], Co^{2+} -related emission is typically weak, strongly thermally quenched, and associated with low photoluminescence quantum efficiency. These limitations originate from two intrinsic factors: the strong coupling of Co^{2+} d-d excited states to lattice vibrations in high-phonon-energy environments, which facilitates rapid multiphonon nonradiative relaxation [18], and the low electric-dipole allowance of spin-forbidden transitions under octahedral or near-cubic crystal fields. As a result, Co^{2+} -centered luminescence is extremely sensitive to local coordination geometry and the surrounding structural landscape.

To mitigate the limitations discussed above, increasing attention has been directed toward tetrahedrally coordinated $[CoX_4]^{2-}$ ($X = Cl, Br, I$) units [19]. In a tetrahedral crystal field, the splitting scheme and selection rules of Co^{2+} are substantially modified, enabling enhanced d-p mixing and increased optical allowance in the visible region. A number of molecular crystals and hybrid halides incorporating isolated $[CoX_4]^{2-}$ tetrahedra have been reported, including $(C_5H_{14}N_2)[CoCl_4] \cdot 0.5H_2O$ [20], $[4-FBzTPP]_2[CoBr_4]$ [21], and $[2-NO_2BzTPP]_2[CoBr_4]$ [9], among others. In these systems, the spatial separation of $[CoX_4]^{2-}$ units by organic frameworks leads to highly localized electronic structures, and detectable visible emission dominated by Co-centered excited states has indeed been observed in selected cases. These results highlight the potential of isolated cobalt halide tetrahedra as luminescent building blocks in hybrid halides. Beyond the inorganic coordination environment, the organic sublattice in hybrid halides provides an additional and powerful handle for regulating excited-state behavior [22]. The size, rigidity, and packing characteristics of organic cations determine the local free volume and configurational relaxation space available to the inorganic clusters, thereby influencing electron-phonon coupling strength, excited-state localization, and nonradiative dissipation pathways [23,24]. In parallel, the introduction of secondary metal ions into low-dimensional halide frameworks offers further opportunities to tailor local electronic environments and interaction ranges. In particular, ns^2 -type metal ions are known to exhibit strong polarizability and stereochemical activity, which can substantially reshape the local potential landscape experienced by neighboring luminescent centers.

Despite these advances, hybrid halides employing $[CoBr_4]^{2-}$ tetrahedra as the primary luminescent units remain exceedingly rare. Most existing studies involving cobalt have instead focused on Co^{2+} -doped lead halide nanocrystals or wide-bandgap perovskites, where cobalt typically acts as a dopant to modulate magneto-optical responses or introduce additional absorption channels, as exemplified by Co-doped $MAPbBr_3$ and $CsPbCl_3$

[25,26]. In such cases, the local structure and optical behavior of Co^{2+} are largely dictated by the lead-halide host lattice, making it difficult to isolate intrinsic Co-centered excited-state characteristics. By contrast, systems constructed directly from $[\text{CoX}_4]^{2-}$ frameworks offer a more suitable platform for elucidating how structural confinement, local interactions, and external perturbations govern cobalt-centered luminescence. Nevertheless, two critical aspects remain insufficiently explored: (i) the role of compositional doping as an independent and systematically tunable parameter for regulating the localization and relaxation of Co-centered excited states, and (ii) the comparative influence of organic cation architecture on local structural confinement, interaction range, and electron-phonon coupling around $[\text{CoBr}_4]^{2-}$ units.

Based on the considerations, two phosphonium-type organic cations, benzyl triphenyl phosphonium (BTP^+) and triphenyl phosphonium (PPh_3^+), were selected as structural modulation units to construct 0D hybrid halide frameworks featuring isolated $[\text{CoBr}_4]^{2-}$ tetrahedra as the luminescent cores, namely $(\text{BTP})_2\text{CoBr}_4$ and $(\text{PPh}_3)_2\text{CoBr}_4$. On this basis, Pb^{2+} ions with an ns^2 electronic configuration are then introduced as a secondary component to modulate the local electronic and structural environment of the cobalt halide framework while preserving its zero-dimensional architecture. Focusing on the differences in organic frameworks and doping modulation, this study conducts a comparative investigation of the luminescent behavior of the materials and their temperature and magnetic field responses, with an emphasis on the formation and evolution of Co-centered excited states under different conditions.

2. Materials and Methods

Lead bromide (PbBr_2 , 99.95%), cobalt bromide (CoBr_2 , 99.0%), triphenyl phosphine (PPh_3 , 99.0%), benzyl triphenyl phosphonium bromide (BTP , 98.0%), methanol (CH_3OH , 99.9%), and hydrobromic acid (HBr , 48 wt% in water) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). All chemicals were used as received without further purification.

2.1. Synthesis of Pb^{2+} -Doped $(\text{BTP})_2\text{CoBr}_4$ Single Crystals

A series of Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$ single crystals were grown by controlled solvent evaporation. BTP (2 mmol), CoBr_2 (1 mmol), and PbBr_2 (x mmol; $x = 10\sim 240\%$) were combined in a 100 mL beaker. BTP was first dissolved in CH_3OH (15 mL), after which HBr (2 mL) was introduced to dissolve CoBr_2 and PbBr_2 . The solution was kept at 80°C and allowed to evaporate slowly for ~ 5 h to yield dark-blue block crystals. The crystals were washed with *n*-hexane to remove unreacted organic precursors and excess phosphonium species that are soluble in nonpolar solvents and then dried under vacuum at 60°C for 12 h prior to characterization. The phase purity of the obtained products was confirmed by PXRD analysis.

2.2. Synthesis of Pb^{2+} -Doped $(\text{PPh}_3)_2\text{CoBr}_4$ Single Crystals

Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$ single crystals were prepared using a solvothermal method. PPh_3 (2 mmol), CoBr_2 (1 mmol), and PbBr_2 (x mmol; $x = 10\sim 190\%$) were loaded into a Teflon-lined stainless-steel autoclave, followed by the addition of 5 mL of HBr . The mixture was ultrasonicated for 5 min to ensure homogeneity, then sealed and heated at 180°C for 8 h. After the reaction, the autoclave was cooled to room temperature at a controlled rate of $5^\circ\text{C}\cdot\text{h}^{-1}$. Dark-blue single crystals were collected, washed with *n*-hexane to remove residual organic species and excess phosphonium components soluble in nonpolar solvents, and dried at 60°C for 12 h, yielding Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$ single crystals suitable for further characterization.

3. Results and Discussion

3.1. Structural Analysis

The crystal structures of $(\text{BTP})_2\text{CoBr}_4$ and $(\text{PPh}_3)_2\text{CoBr}_4$ were determined by single-crystal X-ray diffraction (SCXRD). $(\text{BTP})_2\text{CoBr}_4$ crystallizes in the triclinic system with space group $P-1$ (Table S1), whereas $(\text{PPh}_3)_2\text{CoBr}_4$ adopts a monoclinic structure with space group $P2_1/c$ (Table S2). As shown in Figure 1a,d, both compounds are constructed from isolated $[\text{CoBr}_4]^{2-}$ tetrahedra serving as the inorganic building units. Notably, although the inorganic cores are identical, their surrounding organic environments differ markedly. In $(\text{BTP})_2\text{CoBr}_4$, the presence of flexible benzyl moieties endows the framework with greater configurational freedom. In contrast, the more compact PPh_3^+ cations tend to form dense π - π stacking interactions, resulting in a more rigid local structural environment. Such differences in the organic frameworks are expected to directly influence the local crystal-field strength and distortion of the $[\text{CoBr}_4]^{2-}$ tetrahedra, thereby providing a structural basis for the distinct photophysical behaviors observed in the two systems.

As shown in Figure 1b,e, the experimental powder X-ray diffraction (PXRD) patterns of the bulk samples are in excellent agreement with those simulated from the corresponding SCXRD data, confirming the high phase purity of the as-prepared single crystals. No extra diffraction peaks attributable to secondary phases are observed, indicating that the obtained crystals faithfully represent the intrinsic crystal structures of the target compounds. Further insight into the incorporation of Pb^{2+} was obtained from the PXRD patterns collected at different doping levels (Figure S1). With the gradual introduction of Pb^{2+} , no new diffraction peaks or peak splitting are detected in either system, while the main diffraction peaks exhibit a continuous shift toward lower diffraction angles. This systematic low-angle shift is consistent across both series and becomes more pronounced with increasing Pb^{2+} content. Considering the significantly larger ionic radius of Pb^{2+} (1.19 Å) compared to that of Co^{2+} (0.72 Å), such a trend can be reasonably attributed to the partial incorporation of Pb^{2+} into local sites in or around the $[\text{CoBr}_4]^{2-}$ tetrahedra, leading to a slight lattice expansion. Although the overall peak shifts remain small, their continuous and monotonic evolution with increasing doping level suggests that Pb^{2+} incorporation occurs in a localized and limited manner rather than through large-scale substitution. Nevertheless, this degree of local incorporation is sufficient to effectively modulate the local crystal-field environment of the $[\text{CoBr}_4]^{2-}$ units, which is crucial for the subsequent tuning of their photophysical properties [27].

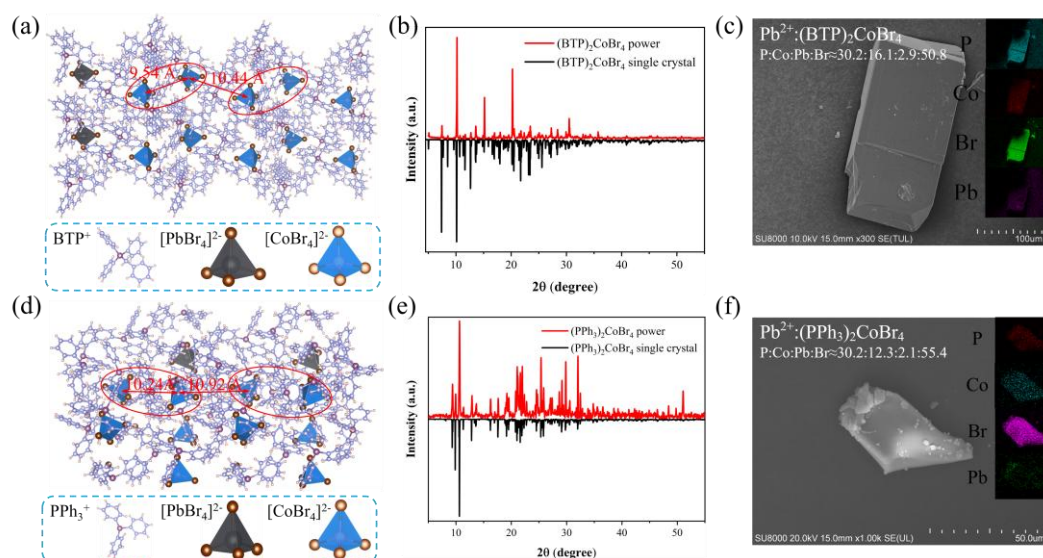


Figure 1. Single-crystal structures of (a) $(\text{BTP})_2\text{CoBr}_4$ and (d) $(\text{PPh}_3)_2\text{CoBr}_4$ determined by SCXRD; comparison between experimental PXRD patterns and simulated patterns derived from the corresponding SCXRD data for (b) $(\text{BTP})_2\text{CoBr}_4$ and (e) $(\text{PPh}_3)_2\text{CoBr}_4$; Scanning electron microscopy (SEM) images and corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping results of (c) Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$ and (f) Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$.

To further confirm the successful incorporation of Pb^{2+} and its chemical state, X-ray photoelectron spectroscopy (XPS) measurements were performed, with detailed spectra provided in the Supporting Information (Figure S2). Compared with the pristine sample, the Pb-doped sample exhibits clear Pb 4f signals, while the Co 2p and Br 3d signals remain essentially unchanged in both peak position and shape. This observation indicates that the introduction of Pb does not disrupt the primary $[\text{CoBr}_4]^{2-}$ framework but instead occurs in a locally accommodated manner within the lattice. The binding energies of the Pb 4f doublet are consistent with the divalent oxidation state of Pb^{2+} , and no signatures corresponding to metallic Pb or higher-valence Pb species are detected, confirming the chemical stability of Pb in the host lattice. The elemental composition and spatial distribution were further examined by EDS. As shown in Figures 1c,f and S3, Co, Br, and P elements are homogeneously distributed across the selected regions. For the Pb-doped samples, Pb is likewise uniformly dispersed without any detectable segregation, and no evidence of Pb-rich domains or secondary Pb-Br phases is observed. The absence of impurity peaks in PXRD patterns, together with the uniform EDS mapping results, excludes the formation of separate Pb-containing phases. By combining the semiquantitative results obtained from XPS with the elemental ratios derived from EDS analysis, the relative proportions of Co, Br, P, and Pb in the doped samples are found to be in good agreement with the nominal precursor ratios and the proposed solid-solution model, approaching an overall stoichiometry of approximately 2:1:4. These results further indicate that the incorporation of Pb^{2+} is stable and controllable and does not induce pronounced phase separation within either system.

3.2. Optical Properties

Figure 2a,b present the photoluminescence (PL), photoluminescence excitation (PLE), and absorption spectra of Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$ and Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$. Both systems exhibit clear and stable multipeak emission features in the visible region, mainly distributed between 400 and 550 nm. The good reproducibility of these multipeak structures among different samples indicates that the observed emission does not originate from accidental defect states but is instead governed by intrinsic and repeatable localized excited states of the system. The corresponding PLE spectra show that the dominant excitation bands of both materials strongly overlap with the absorption edge near ~365 nm, suggesting that the emission process is closely associated with excited states near the band edge. Combined with the spectral evolution at different Pb^{2+} doping levels (Figure S4), it can be seen that increasing the Pb^{2+} feeding ratio leads to a pronounced enhancement in emission intensity, while the emission peak positions and spectral profiles remain essentially unchanged. Therefore, unless otherwise specified, subsequent discussions focus on samples with the optimal luminescence performance. By contrast, the undoped samples exhibit almost no detectable emission in the visible region (Figure S5), which is consistent with the typical behavior of high-spin Co^{2+} in tetrahedral halide crystal fields, where the d-d excited states are spin-forbidden and readily relax through nonradiative pathways under strong electron-phonon coupling, resulting in luminescence quenching. Upon Pb^{2+} incorporation, visible emission absent in the pristine samples emerges in both systems, indicating that Pb^{2+} plays an important role in suppressing nonradiative relaxation and activating radiative transitions [28,29]. In terms of emission composition, the

visible luminescence is mainly composed of two emission bands centered at approximately 450 and 500 nm. The emission band at 450 nm can be attributed to d-d transitions associated with short-range Co-Co FM interactions, whereas the 500 nm emission is more consistent with the DAP-type transition introduced by the Co-Pb configuration [30]. In previously reported tetrahedral Co^{2+} halide systems, d-d transitions are typically too weak to be detected due to dominant nonradiative relaxation. The present results indicate that controlled dopant-induced modulation can partially alleviate this limitation in Co-based halide frameworks. Notably, the absorption edge of the BTP-based system is slightly red-shifted relative to that of the PPh_3 -based counterpart, reflecting the different local structural environments imposed by the two organic frameworks and their modulation of the Co-Br coordination environment and local potential landscape. Although the two systems exhibit similar emission profiles at room temperature, the differences in spatial confinement and local interactions provided by the organic frameworks establish a structural basis for the divergent excited-state evolution observed at low temperatures.

As shown in Figure 2c, the time-resolved photoluminescence (TRPL) decay curves of both materials can be well fitted by a single-exponential function, indicating that the emission dynamics are dominated by a single type of localized excited state. The lifetime of the BTP-based compound ($\tau_{\text{BTP}} = 20.92$ ns) is notably longer than that of the PPh_3 -based counterpart ($\tau_{\text{PPh}_3} = 14.65$ ns). The longer lifetime observed in the BTP framework can be attributed to its larger molecular volume and higher polarizability, which partially suppress nonradiative relaxation pathways of the Co-centered excited states. By contrast, the more compact and rigid PPh_3 framework enhances local structural confinement, facilitating stronger coupling between the excited states and lattice vibrations, thereby accelerating excited-state dissipation and resulting in a shorter lifetime. Notably, the lifetime difference is consistent with the vibrational characteristics observed in the PL spectra. The BTP-based system exhibits more clearly resolved vibronic fine structures, reflecting strong electron-phonon coupling while maintaining radiative recombination as the dominant decay channel. In comparison, the PPh_3 -based system shows faster excited-state depletion, indicative of more efficient nonradiative relaxation.

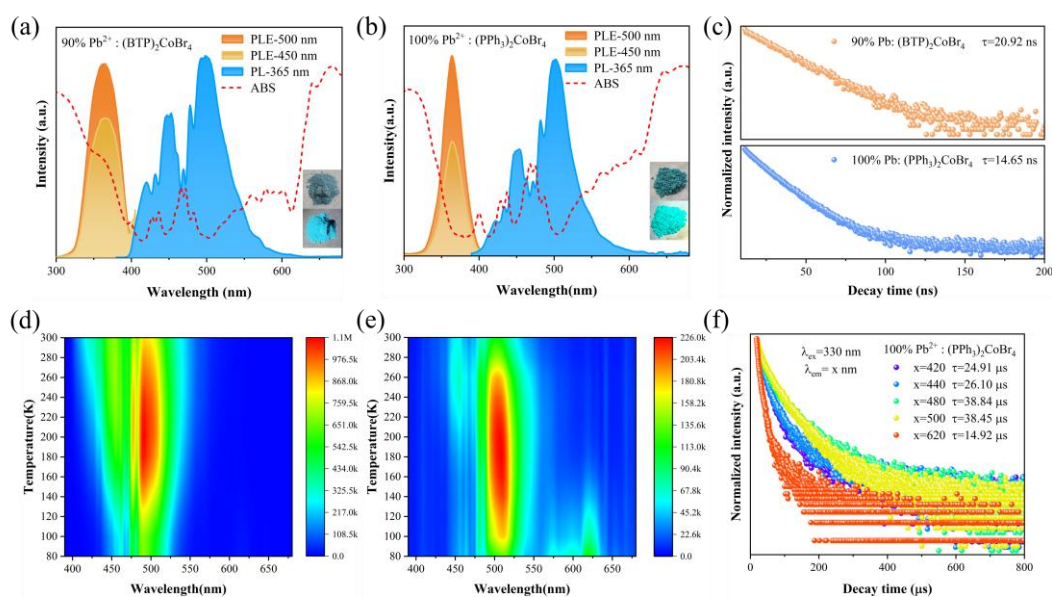


Figure 2. Photoluminescence behaviors of Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$ and Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$: (a,b) PL, PLE, and absorption spectra (the inset shows photographs of the samples before and after excitation under 365 nm ultraviolet light); (c) room-temperature TRPL decay curves; (d,e) temperature-dependent PL spectra presented as pseudocolor maps; (f) wavelength-dependent TRPL decays of Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$ measured at low temperature.

Temperature-dependent photoluminescence (PL) spectra (Figure 2d,e) reveal both shared features and distinct differences in the localized excited-state dynamics of the two Pb^{2+} -doped $[\text{CoBr}_4]^{2-}$ systems. For Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$, the emission is mainly located in the 400–550 nm range and consists of a set of multipeak features centered around ~500 nm. The overall spectral profile remains essentially unchanged from 80 to 300 K, apart from a slight red shift. As the temperature increases from 80 K to approximately 200 K, the integrated emission intensity in the ~500 nm region gradually increases and reaches a maximum near 200 K. Upon further heating to room temperature, the emission intensity decreases slowly without exhibiting any abrupt quenching behavior. This nonmonotonic temperature dependence suggests that, at low temperatures, a fraction of photoexcited carriers is trapped in deeper localized states or defect-related traps, which limits their participation in radiative recombination through the $[\text{CoBr}_4]^{2-}$ -related emission channel. With increasing temperature, thermal activation enables the release of carriers from these localized states, allowing them to re-enter the radiative recombination process and resulting in maximized emission around 200 K. At higher temperatures, phonon-assisted nonradiative relaxation becomes progressively more pronounced, leading to a gradual reduction in emission intensity. Meanwhile, the emission lifetime shows only limited variation over the entire temperature range, indicating that the dominant emission originates from the same type of localized excited state throughout, with temperature mainly modulating the relative balance between radiative and nonradiative relaxation pathways.

In contrast, Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$ exhibits markedly different luminescence behavior at low temperatures. In addition to retaining multipeak emission in the 400–550 nm range similar to that observed in the BTP-based system, an additional orange emission band centered at approximately 620 nm emerges at low temperatures. The corresponding lifetime reaches several tens of microseconds (Figure 2f), which is significantly longer than the nanosecond-scale lifetime observed in the ~500 nm region. This low-energy emission is particularly pronounced at a Pb^{2+} feeding ratio of 70% (Figure 3a) and becomes the dominant emission channel in the temperature range of 80–140 K. Upon increasing the temperature, this low-energy emission rapidly decays and nearly disappears around 200 K, exhibiting a clear low-temperature selectivity. This pronounced difference indicates that the 620 nm emission observed at low temperatures corresponds to an excited state with a lower energy level and a higher degree of localization. Such an excited state is stabilized only under low-temperature conditions and is fundamentally different in physical origin from the excited-state processes that dominate the emission at room temperature.

To further elucidate the origin of this low-temperature emission branch, temperature-dependent structural and magnetic characterizations were carried out on Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$. As shown in Figure S8, the temperature-dependent XRD results indicate no evident structural phase transition between 300 and 120 K, while systematic shifts of selected diffraction peaks toward higher angles upon cooling indicate continuous lattice contraction at low temperatures. Such thermal contraction effectively reduces the average separation between neighboring $[\text{CoBr}_4]^{2-}$ tetrahedra, providing a structural basis for enhanced short-range FM interactions. Consistently, the temperature-dependent magnetic susceptibility curve in Figure 3b reveals a clear deviation from simple paramagnetic behavior at low temperatures, accompanied by an enhancement of magnetic susceptibility, indicating progressively strengthened exchange interactions between adjacent Co^{2+} spins upon cooling. The low-temperature hysteresis loop in Figure 3c further supports this trend, showing a significantly enhanced magnetic response at 90 K compared with room temperature, although long-range magnetic ordering is not established. The intrinsic connection between the structural and magnetic changes and the low-temperature luminescent behavior is further corroborated by the low-temperature magneto-photoluminescence data in Figure 3d. At 11.5 K, the broadband emission centered at ~620 nm exhibits a

pronounced intensity response to the applied magnetic field, with its overall intensity decreasing noticeably as the field varies. In contrast, the multippeak emission near ~500 nm shows only a relatively minor change in overall intensity, while its spectral shape remains essentially unchanged [31].

By correlating the temperature-dependent PL, structural, magnetic, and magnetic-field-dependent luminescence results, it can be inferred that in Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$, lattice contraction at low temperatures significantly reduces the spatial separation between neighboring $[\text{CoBr}_4]^{2-}$ tetrahedra. This enhanced spatial proximity strengthens short-range ferromagnetic exchange interactions, leading to the formation of magnetic bipolaron for emission [32]. This magnetic bipolaron manifests as a long-lived emission branch centered at approximately 620 nm and exhibits high sensitivity to an external magnetic field. Magnetic-field-responsive luminescence of this type has been rarely reported in low-dimensional tetrahedral Co^{2+} halide systems. Upon heating, lattice vibrations weaken the exchange interactions and spin polarization, leading to rapid destabilization and disappearance of this emission channel. By contrast, the larger spatial separation imposed by the BTP^+ framework suppresses effective short-range magnetic exchange between neighboring $[\text{CoBr}_4]^{2-}$ units at low temperature; consequently, no analogous magnetically related luminescence is observed. By contrast, the larger spatial separation imposed by the BTP^+ framework prevents the establishment of effective short-range magnetic exchange between neighboring $[\text{CoBr}_4]^{2-}$ units at low temperature; consequently, no analogous magnetically related luminescence is observed.

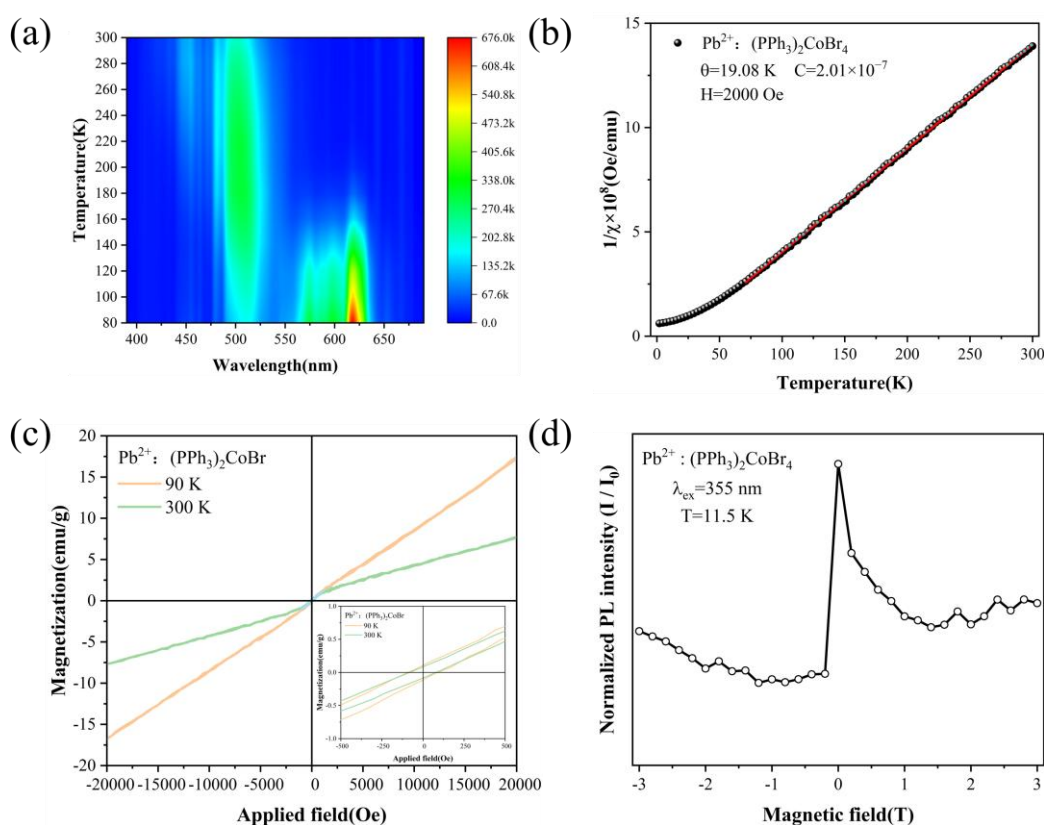


Figure 3. Characterization of Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$: (a) Pseudocolor map of the temperature-dependent PL spectra; (b) Temperature-dependent magnetic susceptibility, with Curie-Weiss fitting yielding parameters ($1/\chi = (T - \theta)/C$); (c) Magnetization (M-H) curves at different temperatures, with the inset showing the detailed low-field region; (d) Low-temperature magneto-photoluminescence spectra.

Figure S9 presents the low-frequency Raman spectra of four representative samples in the range of 0–500 cm^{-1} . All samples exhibit a strong and well-defined vibrational band at approximately 89–91 cm^{-1} , which can be assigned to external lattice modes of the $[\text{CoBr}_4]^{2-}$ tetrahedra, corresponding to collective rocking or twisting motions of the inorganic framework. Notably, the position of this mode remains unchanged regardless of the organic cation type or Pb^{2+} doping level, indicating that the $[\text{CoBr}_4]^{2-}$ tetrahedra constitute a common and structurally robust building unit in both material systems. Upon Pb^{2+} doping, this low-frequency mode shows a clear increase in intensity accompanied by slight linewidth broadening, suggesting enhanced local distortion of the inorganic framework and an increased lattice polarizability. These changes reflect a strengthening of the coupling between the Co-Br coordination environment and lattice phonons. In addition, several weaker Raman features appearing in the 150–300 cm^{-1} region can be attributed to bending or deformation modes of the Co-Br bonds. These modes exhibit similar characteristics, namely enhanced intensity without appreciable peak shifts, further supporting the picture of increased lattice distortion without a fundamental change in local coordination geometry. Importantly, these Raman-active vibrational modes show a close correspondence with the vibronic fine structures observed in the PL spectra, providing independent evidence that the emission processes in these Pb^{2+} -doped systems are governed by strong electron-phonon coupling.

3.3. Energy Band Calculations

To gain further insight into the differences in the luminescence behaviors of the two $[\text{CoBr}_4]^{2-}$ -based hybrid halide systems, first-principles density functional theory (DFT) calculations were performed for both the pristine and Pb^{2+} -doped compounds. The calculated electronic band structures and corresponding density of states reveal that, for both systems, the valence band maximum (VBM) and conduction band minimum (CBM) are located at the same point, indicating a direct bandgap character. Notably, the energy bands near the band edges exhibit extremely weak dispersion and narrow bandwidths, suggesting that the electronic states at the band edges are highly localized in real space. This pronounced localization of band-edge states is fully consistent with the experimentally observed weak carrier transport, the presence of pronounced vibronic fine structures in the emission spectra, and the dominance of localized excited states in the radiative recombination processes.

From the calculated band structures shown in Figure 4a,c,e,g, the theoretical band gaps of the undoped $(\text{BTP})_2\text{CoBr}_4$ and $(\text{PPh}_3)_2\text{CoBr}_4$ are approximately 1.36 eV and 1.43 eV, respectively. Upon Pb^{2+} doping, the band gaps are reduced to about 1.05 eV for $(\text{BTP})_2\text{CoBr}_4$ and 1.16 eV for $(\text{PPh}_3)_2\text{CoBr}_4$. These values are in good agreement with the bandgap energies extracted from Tauc analysis of the experimental absorption spectra (Figure S10), where weak absorption shoulders appear in the visible-to-near-infrared region, yielding optical gaps of approximately 1.56–1.60 eV [33,34]. Similar sub-bandgap absorption features and their influence on optical bandgap analysis have been systematically discussed in low-dimensional metal halide systems [32]. By contrast, the steep absorption onset observed in the ultraviolet region at 3–4 eV can be attributed to ligand-centered π – π^* transitions and high-energy $\text{Br} \rightarrow \text{Co}$ charge-transfer processes [35]. These transitions do not represent the intrinsic optical bandgap of the materials and therefore cannot be used to account for the Pb^{2+} -activated luminescence behavior. Instead, the low-energy absorption shoulders in the visible region are much closer to the DFT-calculated band gaps, indicating that the lowest-energy electronic transitions are indeed dominated by intrinsic localized states associated with the $[\text{CoBr}_4]^{2-}$ tetrahedra. Pb^{2+} doping further enhances this transition pathway by downshifting the conduction band minimum, thereby facilitating radiative recombination through these localized states.

In the doped systems, the incorporation of Pb^{2+} markedly alters the electronic-state composition in the conduction-band region. As revealed by the projected density of states (PDOS) shown in Figure 4b,d,f,h, Pb 6s orbitals strongly hybridize with Co 3d (e_g) and Br 4p states near the CBM, giving rise to new Co-Br-Pb antibonding states in both $(\text{BTP})_2\text{CoBr}_4$ and $(\text{PPh}_3)_2\text{CoBr}_4$. The participation of Pb 6s states in the formation of the CBM has two important consequences. First, it leads to an overall downshift of the CBM, resulting in a pronounced bandgap narrowing from $\sim 1.36/1.43$ eV in the undoped compounds to $\sim 1.16/1.05$ eV upon Pb^{2+} doping. Second, the increased Pb-derived p-character at the band edge enhances the electric-dipole-allowed nature of the lowest excited states, thereby increasing the radiative transition probability. As a result, Co^{2+} -related excited states that are otherwise strongly forbidden and prone to nonradiative quenching become optically active, giving rise to stable and intense visible emission in the doped samples.

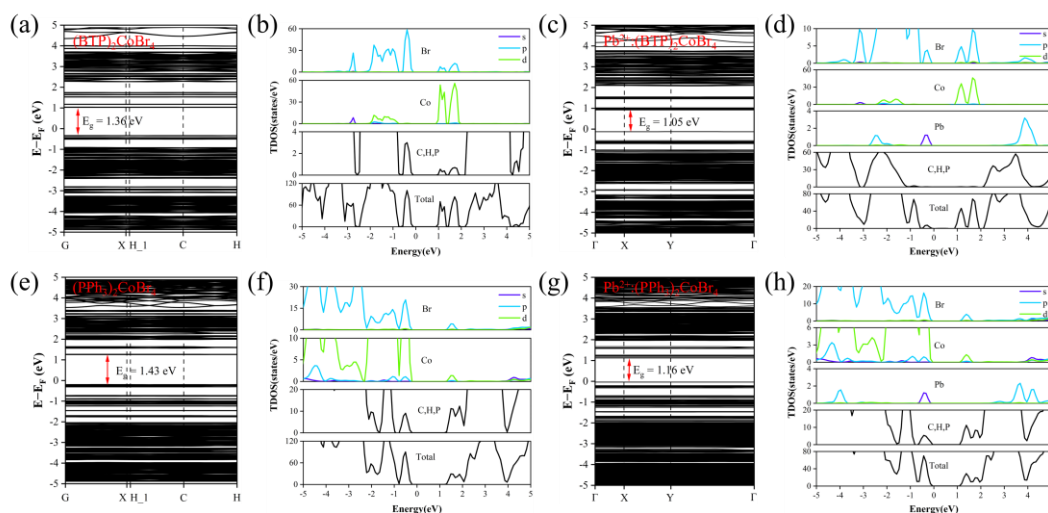


Figure 4. Calculated electronic band structures and corresponding PDOS for pristine and Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$ ((a,b) and (c,d), respectively) and pristine and Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$ ((e,f) and (g,h), respectively).

Figure 5a,b show the two distinct optical processes of Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$ and Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$. Both systems exhibit stable visible light emission at room temperature, consisting primarily of two emission bands centered at approximately 450 nm and 500 nm. Combining the spectral features, lifetime behaviors, and structural environments, it is evident that these two emissions originate from different physical processes. The emission at 450 nm arises from Co^{2+} d-d transitions, representing a typical single-center localized radiative process. In the undoped samples, due to the spin-forbidden nature of high-spin Co^{2+} d-d excited states and strong electron-phonon coupling, this transition channel primarily relaxes via non-radiative pathways, making it difficult to observe effectively. The introduction of Pb^{2+} does not alter the intrinsic energy levels of this transition, but by adjusting the local lattice polarization and energy dissipation environment, it weakens the non-radiative relaxation pathway, granting this otherwise quenched d-d transition a limited but detectable radiative probability, leading to the formation of the 450 nm emission signal in the visible region. In addition to the d-d emission, a 500 nm emission band also appears in the Pb^{2+} doped samples. This emission does not arise from a simple Co^{2+} internal transition process. It can be attributed to the DAP transition induced by Pb^{2+} incorporation, where Co serves as the donor and Pb acts as the acceptor. The excited electrons undergo radiative recombination between Co and Pb, providing a new pathway for the previously restricted excited states, thus forming the 500 nm emission.

In these unified inorganic luminescent centers, the organic cations BTP^+ and PPh_3^+ shape the local potential surfaces differently and adjust the interactions between the cobalt tetrahedra. In the BTP^+ system, the larger organic cations create a more restricted local environment around the inorganic clusters, making it difficult for $[\text{CoBr}_4]^{2-}$ to undergo significant structural rearrangement after excitation. As a result, the excited state remains within the first potential well and relaxes back to the ground state via the radiative emission channel, forming stable and regular multi-peak emission. In contrast, in the more compact PPh_3^+ system, the larger local relaxation space allows the excited state to further relax along the configuration coordinate, which reduces the distance between the cobalt tetrahedra at low temperatures, enhancing short-range FM interactions. This promotes the formation of magnetic bipolaron for emission, leading to long-lived wide-band emission at approximately 620 nm [36,37].

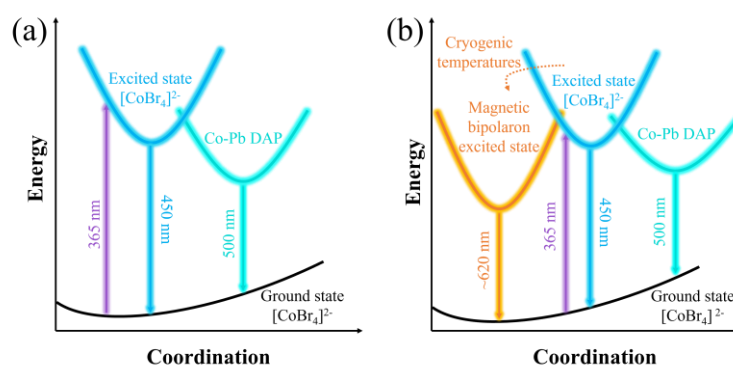


Figure 5. Schematic illustration of the photophysical processes in (a) Pb^{2+} -doped $(\text{BTP})_2\text{CoBr}_4$ and (b) Pb^{2+} -doped $(\text{PPh}_3)_2\text{CoBr}_4$.

4. Conclusions

This study focuses on the design and construction of two types of 0D organic-inorganic hybrid cobalt halide systems based on $[\text{CoBr}_4]^{2-}$ inorganic clusters and successfully activates the traditionally inefficient Co^{2+} systems for visible light emission by introducing small amounts of Pb^{2+} . The results show that in the undoped pure samples, the emission is limited due to spin polarization and local structural constraints, exhibiting self-quenching behavior. Pb^{2+} doping induces modifications in the electronic structure, particularly involving reconstruction near the conduction-band minimum and activation of localized states associated with the $[\text{CoBr}_4]^{2-}$ units, thereby converting $[\text{CoBr}_4]^{2-}$ from an originally non-emissive state into a visible emissive state. This demonstrates that by properly tuning the local crystal field and coordination environment, the traditional d-d emission limitations in transition metal halides can be overcome, opening up new strategies for the activation of cobalt-based luminescence.

Moreover, the study reveals that the size of the organic framework has a significant effect on the relaxation dynamics and emission properties of the excited states. The BTP^+ framework, by restricting local freedom, forms stable multi-peak emission, while the PPh_3^+ framework, with greater local freedom, promotes the formation of magnetic bipolaron for emission, leading to long-lived emission centered around ~620 nm. In conclusion, this study represents a breakthrough in cobalt halide systems from the “almost non-emissive high-spin Co^{2+} system” to the “engineerable $[\text{CoBr}_4]^{2-}$ emission units” and provides a clear mechanism for the cooperative regulation of localized excited states by Pb^{2+} doping and organic cations, offering important theoretical insights for the design and optimization of Co-based halide perovskite materials in the future.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app16052330/s1>, Table S1: Crystal data and structure refinement for (BTP)₂CoBr₄; Table S2 Crystal data and structure refinement for (PPh₃)₂CoBr₄; Table S3 The amount of Pb, Br, P and Co in (BTP)₂CoBr₄ and 90%Pb: (BTP)₂CoBr₄; Table S4 Elemental composition of (PPh₃)₂CoBr₄ and 100%Pb: (PPh₃)₂CoBr₄ determined by EDS; Figure S1: Single-crystal structures of (a) (BTP)₂CoBr₄ and (b) (PPh₃)₂CoBr₄ determined by SCXRD; (c) Packing diagram of (PPh₃)₂CoBr₄ highlighting the offset π - π stacking interactions between adjacent phenyl rings. The centroid-centroid distance is 3.57 Å; (d, e) PXRD patterns of (BTP)₂CoBr₄ and (PPh₃)₂CoBr₄ with different Pb²⁺ doping concentrations; (f) comparison between the SCXRD patterns of (BTP)₂CoBr₄ and (PPh₃)₂CoBr₄; Figure S2: XPS analysis of pristine (BTP)₂CoBr₄ and Pb²⁺-doped (BTP)₂CoBr₄: (a) XPS survey spectra; high-resolution XPS spectra of (b) P 2p, (c) Br 3d, (d) Co 2p and (e) Pb 4f; Figure S3: SEM images and corresponding EDS elemental mapping of (a) (BTP)₂CoBr₄ and (b) (PPh₃)₂CoBr₄; Figure S4: PL and PLE spectra of (a, b) (BTP)₂CoBr₄ (inset displays the near-infrared spectra of the samples.) and (d, e) (PPh₃)₂CoBr₄ with different Pb²⁺ doping concentrations; (c) comparison of the PL spectra of Pb²⁺-doped (BTP)₂CoBr₄ and Pb²⁺-doped (PPh₃)₂CoBr₄; (f) PL, PLE, and absorption spectra of BTP and PPh₃; Figure S5: Photographs of (a, b) (BTP)₂CoBr₄ and (c, d) (PPh₃)₂CoBr₄ samples taken before and after ultraviolet excitation at 365 nm; Figure S6: UV-vis absorption spectra of (a) (BTP)₂CoBr₄ and (b) (PPh₃)₂CoBr₄ with different Pb²⁺ doping concentrations; Figure S7: Room-temperature TRPL decay curves of (a) (BTP)₂CoBr₄ and (b) (PPh₃)₂CoBr₄ with different Pb²⁺ doping concentrations; Figure S8: (a) Temperature-dependent PL spectra of 90% Pb²⁺-doped (BTP)₂CoBr₄; (b) Low-temperature TRPL decay curves of 90% Pb²⁺-doped (BTP)₂CoBr₄ monitored at different emission wavelengths; (c) Temperature-dependent PL spectra of 100% Pb²⁺-doped (PPh₃)₂CoBr₄; (d) Temperature-dependent PL spectra of 70% Pb²⁺-doped (PPh₃)₂CoBr₄; (e) Temperature-dependent XRD patterns of 70% Pb²⁺-doped (PPh₃)₂CoBr₄; (f) Pseudocolor map of the low-temperature magneto-photoluminescence spectra of 70% Pb²⁺-doped (PPh₃)₂CoBr₄; Figure S9: Comparison of Raman spectra of (a, b) (BTP)₂CoBr₄ and (c, d) (PPh₃)₂CoBr₄ before and after Pb²⁺ doping; Figure S10: Experimental optical band gaps of (a) (BTP)₂CoBr₄ and (b) (PPh₃)₂CoBr₄ before and after Pb²⁺ doping, extracted from Tauc plots.

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Data Availability Statement: The data presented in this study are available in the article and the Supporting Information, and are available from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

The following abbreviations are used in this manuscript:

FM	Ferromagnetic
DAP	Donor-Acceptor Pair
0D	Zero-Dimensional
BTP	Benzyl Triphenyl Phosphonium
PPh ₃	Triphenyl Phosphonium
SCXRD	Single-Crystal X-Ray Diffraction

PXRD	Powder X-Ray Diffraction
SEM	Scanning Electron Microscopy
EDS	Energy-Dispersive X-ray Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
PL	Photoluminescence
PLE	Photoluminescence Excitation
TRPL	Time-Resolved Photoluminescence
DFT	Density Functional Theory
VBM	Valence Band Maximum
CBM	Conduction Band Minimum
PDOS	Projected Density of States

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