Effect of Donor-Acceptor Concentration Ratios on Non-Radiative Energy Transfer in Zero-Dimensional Cs$_4$PbBr$_6$ Perovskite/MEH-PPV Nanocomposite Thin Films

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Abstract: Composite materials with different concentration ratios of a hybrid of zero-dimensional (0-D) Cs$_4$PbBr$_6$ perovskite, which acts as a donor (D), and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), which acts as an acceptor (A), were successfully prepared via a solution blending method prior to being deposited onto glass substrates by a spin-coating technique. The influence of acceptor content on the structural, optical, and energy transfer properties of the donor was investigated. The perovskite nanocrystals formed thin films without any chemical interactions within a matrix of MEH-PPV in the blend. The possibility of dipole–dipole (non-radiative) energy transfer from the 0-D Cs$_4$PbBr$_6$ to the MEH-PPV was proven. The energy transfer parameters such as $R_o$ (critical distance of the energy transfer), $k_{app}$ (apparent quenching constant), $\Phi_{DA}$ (quantum yield of D in the presence of A), $\tau_{DA}$ (lifetime of D in the presence of A), $P_{DA}$ (probability of energy transfer), $\eta$ (efficiency of energy transfer), $R_{DA}$ (energy transfer radius), $k_{ET}$ (energy transfer rate constant), $T_{DR}$ (total decay rate), $A_O$ (critical concentration of A), and $A_\pi$ (conjugation length) were calculated based on the absorption and emission measurements.

Keywords: 0-D Cs$_4$PbBr$_6$ perovskite; MEH-PPV; optical properties; donor/acceptor; energy transfer

1. Introduction

The good electronic properties of halide materials with a perovskite crystal structure [1] have attracted the attention of researchers who have employed these materials as functional material layers in numerous devices, such as quantum-dot light-emitting diodes (QDLEDs) [2], solar cells [3], photodetectors [4], and resistive random access memory (ReRAM) [5]. Moreover, these materials have been widely used in the fabrication of optoelectronic and photonic thin-film devices [6,7] because of their unique properties, such as the ability to tune their band gap energy by manipulating the halide composition, and their high solubility in polar organic solvents, which enables facile deposition processing. However, a major challenge that needs attention is the chemical and electrical stability of hybrid perovskite materials under ambient atmosphere in typical optoelectronic devices [8,9]. Several solutions have been proposed to overcome this problem, including enhancing the morphology of thin films by a coating engineer [10], encapsulation with moisture-resistant layers [11,12], and mixing and changing the acceptor (A) site cation, with the most common materials being of the form MAPbX$_3$ (methylammonium lead halide) [13].
The incorporation of conjugated polymers as a matrix layer in optoelectronic devices based on perovskites can play a significant role in enhancing the morphology of the films resulting in superior device performance [14,15]. Moreover, through-space or dipole–dipole energy transfer plays a significant role in the donor/acceptor hybrids that have been used to produce optoelectronic devices with high performance efficiency [16–19].

In the current work, zero-dimensional (0-D) Cs$_4$PbBr$_6$ perovskite—acting as a donor (D)—and poly [2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV)—acting as an acceptor (A)—were blended with various A/D ratios by the solution blending method. Then, these blends were prepared as thin films using a spin-coating technique. The structural, morphology, and optical properties, and energy transfer mechanisms of the hybrids of 0-D Cs$_4$PbBr$_6$/MEH-PPV were investigated for the first time, to the best of our knowledge.

2. Experimental Details

2.1. Materials

Poly [2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV, $M_w = 40,000$ g/mol) was purchased from Sigma Aldrich (Saint Louis, MO, USA) and used as received without further purification. High-quality green-emitting zero-dimensional Cs$_4$PbBr$_6$, synthesized by a simple solution-processed chemical method [20] was purchased from Quantum Solutions LLC, King Abdullah University of Science and Technology (KAUST), Kingdom of Saudi Arabia. A toluene solution with a purity of 99.8%, which was produced by Fluka (Buchs, Switzerland), was used to dissolve all the materials.

2.2. Methods

The solution blending method was employed to prepare hybrids of zero-dimensional Cs$_4$PbBr$_6$ and MEH-PPV, which act as the donor and acceptor, respectively. Solutions of various concentration ratios of A/D (where each A and D in mg/ml concentration), namely 0, 0.1, 0.2, 2.0, and 4.0, were prepared. Then, 50 µL samples of each solution were deposited onto glass substrates using a spin-coating technique (2000 rpm for 20 s). All the thin films were annealed at 120 °C in a vacuum oven to remove any remaining solvent.

2.3. Characterization

A Panalytical X’PERT Pro powder X-ray diffractometer (Panalytical, Almelo, The Netherlands) in the $\theta$–2$\theta$ geometry was employed to characterize the sample structure. A Cu-K$_\alpha$ radiation source operated at 40 mA and 45 kV was used in the X-ray diffraction (XRD) measurements, and the scanning angle ($2\theta$) was varied from 10° to 80° with a step size of 0.02° at 0.5° min$^{-1}$. The morphology of the 0-D Cs$_4$PbBr$_6$ and the A/D thin films were investigated by scanning electron microscopy (SEM) (JEOL-7600F, JEOL, Akishima, Japan).

The optical properties of the thin films were investigated by measuring UV–Visible absorption spectra and photoluminescence emission spectra. The UV–Visible spectra were recorded using a V-670 absorption spectrometer (JASCO, Cremella, Italia), whereas the emission spectra were examined using an FP-8200 spectrofluorometer (JASCO, Cremella, Italia) with an excitation wavelength of 350 nm. All the measurements were carried out in the ambient atmosphere.

3. Results and Discussion

3.1. Structural and Morphology of the Hybrid Thin Films

Figure 1 shows the XRD patterns of the 0-D Cs$_4$PbBr$_6$ perovskite thin films with various MEH-PPV ratios (0, 0.1, 0.2, 2.0, and 4.0). The diffraction peaks of the 0-D Cs$_4$PbBr$_6$ perovskite can be indexed at $2\theta = 12.8, 22.7, 25.9, 28.9, 30.5$, and $31.4^\circ$, which correspond to the (110), (300), (024), (214), (223),
and (006) planes. These peaks prove that the 0-D Cs$_4$PbBr$_6$ perovskite exhibited a rhombohedral structure in the R-3c space group (a = b = 13.73 Å, c = 17.32 Å, α = β = 90°, γ = 120°) at ambient conditions [20–22]. These peaks were dramatically reduced in intensity upon increasing the MEH-PPV content and were completely inhibited when the A/D ratio was ≥2.0, where the broadening peak, which corresponds to the amorphous phase of the MEH-PPV, becomes dominant.

![XRD diffractograms](image)

*Figure 1.* XRD diffractograms of 0-D Cs$_4$PbBr$_6$ perovskite thin films with various 2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene (MEH-PPV) ratios.

The morphology of the pristine 0-D Cs$_4$PbBr$_6$ and Cs$_4$PbBr$_6$/MEH-PPV hybrid thin films prepared with A/D ratios of 0.1, 0.2, 2.0, and 4.0 was investigated using SEM images, as shown in Figure 2. The image in Figure 2a shows that the 0-D Cs$_4$PbBr$_6$ perovskite consists of rhombohedral nanocrystals approximately 400 nm in dimension. It can be clearly seen that the perovskite crystals are embedded in a uniform layer of the MEH-PPV (Figure 2b–d). While in the thin film with an A/D ratio of 2.0 (Figure 2c) the MEH-PPV layer is incomplete in certain areas; the thin film with an A/D ratio of 4.0 in Figure 2d displays complete MEH-PPV coverage with no signs of pinholes. Consequently, it can be deduced that the perovskite nanocrystals formed within a matrix of MEH-PPV in the hybrid thin films.
Figure 2. SEM images of the pristine 0-D Cs$_4$PbBr$_6$ and Cs$_4$PbBr$_6$/MEH-PPV hybrid thin films with various ratios. (a) pristine 0-D Cs$_4$PbBr$_6$; (b) 0.1; (c) 0.2; (d) 2.0; (e) 4.0.
3.2. Absorption and Fluorescence Spectra of the Thin Films

The absorption and fluorescence spectra of MEH-PPV and 0-D Cs₄PbBr₆ are presented in Figure 3. The significant overlap between these spectra provides evidence for the possibility of dipole–dipole (non-radiative) energy transfer from the 0-D Cs₄PbBr₆ (donor) to the MEH-PPV (acceptor), which will be investigated in detail in the next section.

![Absorption and fluorescence spectra of MEH-PPV and 0-D Cs₄PbBr₆](image)

**Figure 3.** Overlapping between absorption and fluorescence spectra of MEH-PPV and 0-D Cs₄PbBr₆. Inset: chemical structure of MEH-PPV.

The absorption spectra of the 0-D Cs₄PbBr₆/MEH-PPV hybrid thin films, corresponding to ratios of 0.1, 0.2, 2.0, and 4.0, are illustrated in Figure 4. No new absorbance peak was observed upon increasing the acceptor content, indicating that no aggregates or dimers were formed in the hybrids and no chemical interactions occurred. The absorbance in the wavelength range 600–800 nm, that related to the absorbance of the 0-D Cs₄PbBr₆ [23], was significantly reduced upon increment the MEH-PPV content. Addition of MEH-PPV to Cs₄PbBr₆ shows systematically decrease in broadening absorption spectra in addition to different trend behavior in the absorbance over the entire wavelength range. This observation can be attributed to decreasing conjugation length and possibility of the occurrence of both static and dynamic quenching, as proved here later.

The fluorescence spectra of pristine MEH-PPV and the 0-D Cs₄PbBr₆/MEH-PPV hybrid thin films are shown in Figure 5. When using an excitation wavelength of 350 nm, the main peaks of MEH-PPV and 0-D Cs₄PbBr₆ were detected at 580 and 518 nm, respectively, corresponding to the 0-0 vibrionic transition for each. This excitation wavelength of 350 nm was mainly absorbed by the 0-D Cs₄PbBr₆. As the A/D ratio increased, the 0-D Cs₄PbBr₆ intensity decreased significantly while the related peak intensity of MEH-PPV increased. This observation confirms the possibility of energy transfer from 0-D Cs₄PbBr₆ to MEH-PPV, as acceptor emission made no major contribution under direct excitation at 350 nm.
3.3. Energy Transfer Mechanism

In this study, the possibility of non-radiative energy transfer (Förster-type) can be proven based on four main aspects, namely: (i) the strong overlap (Figure 3) between the fluorescence spectrum of 0-D Cs$_4$PbBr$_6$ perovskite and the absorption spectrum of MEH-PPV; (ii) the strong reduction of the fluorescence intensity of 0-D Cs$_4$PbBr$_6$ perovskite upon the addition of MEH-PPV (as shown in Figure 5); (iii) the improvement of the fluorescence intensity of MEH-PPV (as shown in Figure 5); and (iv) the critical transfer distance between the molecules of 0-D Cs$_4$PbBr$_6$ and MEH-PPV, as calculated later. To describe the energy transfer mechanism between 0-D Cs$_4$PbBr$_6$ and MEH-PPV, various parameters...
were calculated, such as $R_o$ (critical distance of the energy transfer), $k_{app}$ (apparent quenching constant), $\phi_{DA}$ (quantum yield of D in the presence of A), $\tau_{DA}$ (lifetime of D in the presence of A), $P_{DA}$ (energy transfer probability), $\eta$ (energy transfer efficiency), $R_{DA}$ (energy transfer radius), $k_{ET}$ (energy transfer rate constant), $T_{DR}$ (total decay rate), $A_o$ (critical concentration of acceptor), and $A_\pi$ (conjugation length).

The following formula can be employed to calculate the critical distance [24]:

$$R_o^6 = \frac{9000(\ln 10)\beta^2\phi_D}{128\pi^5n^4N_o} \int F_D(\lambda)\epsilon_A(\lambda)\lambda^4d\lambda = \frac{9000(\ln 10)\beta^2\phi_D}{128\pi^5n^4N_o} J(\lambda)$$  \hspace{1cm}(1)

where $n$ is the solvent refractive index, $N_o$ is Avogadro’s number, $\beta^2$ is the orientation factor (0.67 or isotropic media), $\phi_D$ is the donor quantum yield, $\lambda$ is the wavelength, $\epsilon_A(\lambda)$ is the molar decadic extinction coefficient of the acceptor, and $F_D(\lambda)$ is the normalized spectral distribution of the donor (i.e., $\int F_D(\lambda)d\lambda = 1$). The $J(\lambda)$ and $R_o$ values are tabulated in Table 1. The average $R_o$ was 77.54 Å, which confirmed the domination of non-radiative energy transfer (Förster type) in the blends, where the Förster type is typically effective in the range of 10–100 Å [25,26]. Subsequently, as reported by other researchers, this finding confirms the suitability of Förster theory for calculating the energy transfer parameters [27–29].

| A/D Ratio | $\theta_f$ | $k_{nr}$ (ns)$^{-1}$ | $A_\pi$ (Å) | $\tau_f$ (ns) |
|-----------|------------|------------------------|-------------|---------------|
| 0.0       | 0.450      | 0.104                  | -0.201      | 5.30          |
| 0.1       | 0.113      | 0.667                  | -2.057      | 1.33          |
| 0.2       | 0.0484     | 1.670                  | -2.979      | 0.57          |
| 2.0       | 0.0139     | 6.013                  | -4.261      | 0.164         |
| 4.0       | 0.0037     | 22.64                  | -5.586      | 0.044         |

Moreover, the non-radiative energy transfer parameters of the A/D system can be calculated by analyzing its absorption and emission spectra. The following Stern–Volmer equation can be employed to check the type of the emission quenching [30]:

$$\frac{I_D}{I_{DA}} = 1 + k_{app}[A], \quad k_{app} = (k_D + k_S) + k_Dk_S[A]$$  \hspace{1cm}(2)

where $I_{DA}$ and $I_D$ are the emission intensities of D in the presence and absence of A, respectively, $k_D$ & $k_S$ are dynamic and static quenching constants, respectively, and [A] is the acceptor concentration. In many cases, the fluorophore can be quenched both by dynamic and static quenching. A linear Stern–Volmer plot indicates that only one type of quenching occurs, otherwise both types of quenching can occur [30]. Hence, the clear upward curvature shown in Figure 6 indicates that the 0-D Cs$_4$PbBr$_6$ emission is decreased in the presence of MEH-PPV by both static and dynamic quenching. By fitting the data of Figure 6 using the OriginPro 8 program, a theoretical equation was suggested to find the relationship between $\frac{I_D}{I_{DA}}$ and acceptor content as follows:

$$\frac{I_D}{I_{DA}} = 1 + 0.444[A] + 0.0183[A]^2$$  \hspace{1cm}(3)

By comparing this equation with the Stern–Volmer equation, it can be found that $k_D + k_S = 0.444$ µM$^{-1}$ and $k_Dk_S = 0.0183$ µM$^{-2}$. The solutions of these equations are $k_D = 0.40$ µM$^{-1}$ & $k_S = 0.05$ µM$^{-1}$. This indicates that at a MEH-PPV concentration of 20 µM, 50% of the ground-state 0-D Cs$_4$PbBr$_6$ is complexed, and thus is non-fluorescent.
The solutions of these equations are $k = 0, 40$, $R_{\text{o}} = 100 \, \text{Å}$. Furthermore, the distance between molecules of the 0-D Cs$_4$PbBr$_6$ film ($R_{\text{o}}$) was less than 1.5 $R_{\text{o}}$. Consequently, the excited state energy can be transferred through the overlap between donor emission and acceptor absorbance in addition to the enhancement of the dipole-dipole interaction. Therefore, non-radiative energy transfer from 0-D Cs$_4$PbBr$_6$ to MEH-PPV happened with a higher probability for $10 \, \text{Å} < R_{\text{o}} < 100 \, \text{Å}$. Furthermore, the distance between molecules of the 0-D Cs$_4$PbBr$_6$ and MEH-PPV was less than 1.5 $R_{\text{o}}$. These findings are in agreement with previous reports [17,31–33]. Since the distance between donor and acceptor is more than 1 nm, as presented in Table 2, the charge transfer in the current system can be neglected [34]. Moreover, despite the possibility of charge transfer according to the energy levels of both Cs$_4$PbBr$_6$ (HOMO = −5.73 eV, LUMO = −3.40 eV [35]) and MEH-PPV (HOMO = −5.3 eV, LUMO = −3.0 eV [36]), this mechanism can be neglected because of the strong overlap between donor emission and acceptor absorbance in addition to the enhancement of acceptor emission and decrease in that of donor [32,37]. In the Förster energy transfer process, once the Cs$_4$PbBr$_6$ returns to the ground state and then the MEH-PPV is brought to the excited state.
Figure 7. Energy transfer probability for 0-D Cs₄PbBr₆/MEH-PPV hybrid thin films.

Figure 8. Energy transfer efficiency for 0-D Cs₄PbBr₆/MEH-PPV hybrid thin films.

Table 2. Energy Transfer Parameters of the Donor/Acceptor Thin Films.

| A/D Ratio | $J(\lambda) \times 10^{16}$ (M⁻¹ cm⁻¹ nm⁴) | $R_0$ (Å) | $R_{DA}$ (Å) | $k_{ET}$ (ns⁻¹) | $T_{DR}$ (ns⁻¹) |
|-----------|---------------------------------|--------|------------|----------------|----------------|
| 0.1       | 4.97                            | 74.87  | 62.45      | 0.56           | 0.75           |
| 0.2       | 7.66                            | 80.47  | 56.55      | 1.57           | 1.76           |
| 2.0       | 7.49                            | 80.17  | 45.15      | 5.91           | 6.10           |
| 4.0       | 4.88                            | 74.65  | 33.64      | 22.55          | 22.74          |
Figure 9. Energy transfer efficiency vs $R_{DA}/R_0$ for 0-D Cs$_4$PbBr$_6$/MEH-PPV hybrid thin films.

The energy transfer distance between D and A molecules ($R_{DA}$) was based on $R_0$, $I_D$, and $I_{DA}$. Figure 10 displays that as the A/D ratio increased from 0.1 to 4, the $R_{DA}$ decreased from 62.45 to 33.64 Å (Table 2).

The $k_{ET}$ between a single D/A pair separated by $R_{DA}$ can be expressed in terms of $R_0$ as follows [38]:

$$k_{ET} = \frac{1}{\tau_D} \left( \frac{R_0}{R_{DA}} \right)^6$$  \hspace{1cm} (4)

Figure 10. Energy transfer distance vs acceptor (A)/ donor (D) ratio for 0-D Cs$_4$PbBr$_6$/MEH-PPV hybrid thin films.

As listed in Table 2, the values of $k_{ET}$ were significantly enhanced with the increasing A/D ratio. Moreover, the $T_{DR}$ values ($k_{ET} + \tau_D^{-1}$) of the donor upon the addition of acceptor content in the hybrid thin films with various concentration ratios can be summarized in Table 2. As evidenced in earlier
reports [17,30,32] and clearly detected in the present system of D/A hybrids, efficient energy transfer in the hybrids can be confirmed by the increases in both $k_{ET}$ and $T_{DR}$ upon increasing the acceptor content. To suppress intermolecular transfer in the donor, the acceptor concentration should be much lower than $A_o$, which is the acceptor concentration at which 76% of the energy was transferred [29]. The $A_o$ value of the MEH-PPV (~0.96 mM) was estimated based on the average value of $R_0$. On the other hand, the distance between dipoles arising from the ground state to excited singlet state transition can be defined as $A_\pi$ and derived from $k_r$ and $k_{nr}$. No significant variation was observed in the value of $k_r$ (~0.085 ns$^{-1}$) with increasing A/D ratio, whereas the value of $k_{nr}$ increased dramatically with the increasing A/D ratio. Subsequently, $A_\pi$ decreased with the increasing A/D ratio as listed in Table 1.

The exponential relationship between $\Phi_{DA}$ and $A_\pi$, as presented in Figure 11, shows that a new class of hybrids produced from organic/inorganic composites are highly fluorescent.

![Figure 11. Relationship between $\Phi_{DA}$ and $A_\pi$ in 0-D Cs$_4$PbBr$_6$/MEH-PPV hybrid thin films.](image)

4. Conclusions

In the present work, hybrid thin films of 0-D Cs$_4$PbBr$_6$/MEH-PPV with various ratios were successfully prepared by a solution blending method. The form of the perovskite nanocrystals within a matrix of MEH-PPV in the hybrid thin films was determined from XRD and SEM analysis. No chemical interactions occurred between 0-D Cs$_4$PbBr$_6$ and MEH-PPV, as confirmed by XRD and absorption spectra analysis. The dominant energy transfer mechanism in the hybrids was Förster energy transfer, where the average critical distance of the energy transfer ($R_0$) was 77.54 Å. The decrease in the emission of 0-D Cs$_4$PbBr$_6$ with the addition of MEH-PPV was due to both static and dynamic quenching, where 50% of the ground-state 0-D Cs$_4$PbBr$_6$ was complexed and thus, non-fluorescent at 20 µM of MEH-PPV. The hybrid of 0-D Cs$_4$PbBr$_6$/MEH-PPV is promising for use as an emissive layer in optoelectronic devices.

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