New insight into the ultra-long lifetime of excitons in organic–inorganic perovskite: Reverse intersystem crossing

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ARTICLE INFO

ABSTRACT

Recently, an effective exciton diffusion length L exceeding $100\,\mu m$ has been reported for organic–inorganic halide perovskites owing to both the high mobility and ultra-long lifetime of the excitons; however, the origin of ultra-long L is still unclear in nature. In some photoelectric materials, reverse intersystem crossing (RISC) from the triplet to the singlet state can enhance the quantum yield of photoluminescence greatly. In this study, our theoretical investigation indicated that the energy difference ΔE_{st} between the singlet state and the triplet state of $CH_3NH_3PbI_3$ was less than 0.1 eV, which represents one crucial prerequisite for the occurrence of RISC. Meanwhile, the experimental results showed that the photoluminescence lifetime increased with the increasing temperature, a typical feature of RISC. Based on this study, we put forward the hypothesis that the ultra-long lifetime of excitons in organic–inorganic halide perovskite might be caused by the RISC process. This may provide a new insight into the important photophysical properties of such novel photovoltaic materials.

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1. Introduction

As an emerging photovoltaic material, organic–inorganic halide perovskite has attracted considerable attention due to its desirable advantages, such as moderate band gap, facile solution processability, effective exciton dissociation, etc. [1–5]. Despite the high power conversion efficiency of over 20% that has been achieved for perovskite solar cells (PSCs) [6,7], some basic scientific enigmas of this fascinating material require further elaboration; for example, the ultra-long effective charge diffusion length L facilitates the exciton dissociation greatly [8,9]. In general, L is obtained with the following equation:

$$L = \sqrt{D\tau} \tag{1}$$

where τ is the exciton lifetime and D is the charge diffusion coefficient; these two important factors can be determined by transient absorption and photoluminescence-quenching measurements. It is evident that a large value of τ is one prerequisite for an ultra-long L, which has been confirmed experimentally [8,10]. In the mean-time, researchers in this field are willing to determine the origin of these advantageous properties theoretically [11,12].

To date, there have been several explanations for the ultra-long τ of $CH_3NH_3PbI_3$. Based on optical investigations of a single crystal of $CH_3NH_3PbI_3$ from room temperature to 5 K, Fang et al. [13] attributed the ultra-long τ to the bound triplet exciton at temperatures below 160 K, while carriers recombination was induced by spontaneous radiative transitions from band to band at room temperature. On the other hand, Kong et al. [14] found that the longer τ of $CH_3NH_3PbI_3$ originated from free excitons and donor–acceptor-pair transitions. In brief, it can be seen that the early explanations on this issue are ambiguous. In some photoelectric materials, if the energy gap between the singlet and the triplet state is small enough, triplet excitons can return to the singlet state, which is called reverse intersystem crossing (RISC) [15,16]. This important photophysical process helps to increase the exciton's lifetime, which in turn achieves a higher quantum yield [15]. It is important to emphasize that perovskite materials have a periodic structure but to date, no method exists to calculate the excited state of the periodic structure accurately. Our group has proposed a method to deal with the excited state of materials with a periodic structure, such as MOFs [17–19]. To be specific, we selected representative structure units from MOFs by cutting off clusters based on their single crystal structures (obtained from experimental results); the

clusters were calculated after saturation by hydrogen atoms at the boundary. So far, our method has been accepted as a valid strategy to deal with the excited state of periodic structures.

It is known that the singlet–triplet splitting energy (denoted as ΔE_{st} in our work) for inorganic semiconductors and organic molecules varies a lot. The ΔE_{st} of organic molecules has been reported to be 100–200 meV, much larger than that of inorganic materials [15]. $CH_3NH_3PbI_3$ is known as an organic–inorganic hybrid material with many amazing photoelectric properties. Inspired by these investigations, we firstly provided a new insight into the ultra-long τ of $CH_3NH_3PbI_3$ halide perovskite from the perspective of RISC. The experimental results showed that the photoluminescence lifetime increased with the increasing temperature [20,21], a typical feature of RISC. Meanwhile, the ΔE_{st} was then calculated to be 82 meV and 47 meV, which satisfies the prerequisite for the occurrence of RISC in thermally activated delayed fluorescence (TADF) photovoltaic materials [16,22,23]. It is conjectured that, for $CH_3NH_3PbI_3$, the semiconductor properties including ΔE_{st} are highly affected by the organic component. Based on this study, we put forward the hypothesis that the ultra-long lifetime of excitons in organic–inorganic halide perovskite might be caused by the RISC process. Our work provides a new insight into the important photophysical property of these novel photovoltaic materials.

2. Experimental

2.1. Experimental method

102.2 mg $PbCl_2$ and 174.9 mg CH_3NH_3I were weighed. The materials were placed into a sample bottle, 0.5 mL *N,N*-dimethylformamide (DMF) was added and the mixture was heated at 70 °C for 1 h until mixed completely, followed by filtration. The solution and a glass substrate were transferred into a glove box and placed on a heating plate for preheating at 70 °C. After 70 μL of the solution was removed with a pipette, it was spin-coated on the substrate at 2000 rpm/30 s. First, it was heated at 90 °C for 1 h, then it was heated at 100 °C for 25 min, which completed the process for obtaining the $CH_3NH_3PbI_3$ film.

A streak camera (Hamamatsu C10910) was used to obtain the time-resolved photoluminescence (TRPL) spectra and the photoluminescence lifetime of the $CH_3NH_3PbI_3$ film from 80 K to 300 K.

2.2. Computational method

The structure of the $CH_3NH_3PbI_3$ cluster for ground state optimization was cut [24] from the crystal structure [25] of the tetragonal phases, as shown in Fig. 1. The lattice parameters a, b and c are equal to 8.8 Å, 8.8 Å, and 13.0 Å in the periodic tetragonal crystal structure. The lattice parameters α, β and γ are all equal to 90° in the periodic tetragonal crystal structure. According to the symmetry of the crystal structure, a lattice-site unit was cut from the tetragonal $CH_3NH_3PbI_3$ crystal structure to obtain a bigger cluster, namely one-fourth of the octahedral crystal structure. It has been suggested that the $CH_3NH_3^+$ cations in the tetragonal phase still occupy preferred orientations and a certain degree of long-range order [26]. The quantum chemical density functional theory (DFT) and time-dependent density functional theory (TD-DFT) were used to calculate the results using the Gaussian 09 software package [27]. All the atoms except the H atoms were frozen. The basis set Lanl2dz was used including the relativistic effect because Pb atom is heavy. The PBEPBE functional was used to calculate ΔE_{st} in conjunction with the MOMAP-v0.2.003 program developed by Shuai et al. [28–31] to calculate the rate of RISC of $CH_3NH_3PbI_3$. The parameter of the excited states was set to triplet only for the triplet state calculation, i.e., the electrons were excited to the triplet state.
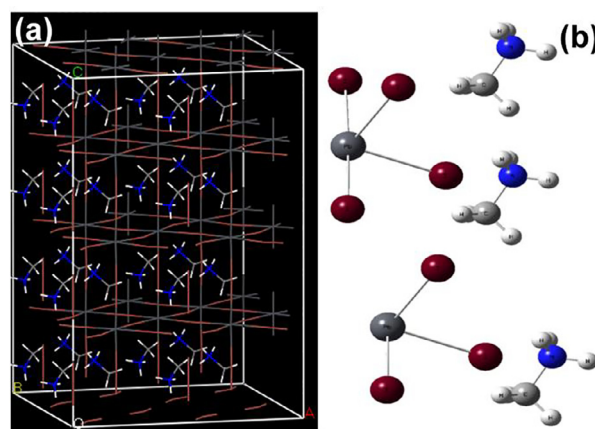

Fig. 1. (a) Tetragonal phases of $CH_3NH_3PbI_3$ crystal structure; (b) Calculative cluster model for ground state cut from the tetragonal crystal. The elements are represented by the following colors: N, blue; C, light gray; H, white; Pb, dark gray; and I, brown.

The peak position of the infrared (IR) spectrum and the maximal absorption in the ultraviolet–visible (UV–vis) spectrum of the $CH_3NH_3PbI_3$ cluster model were matched with the experimental results reported by Ahmed et al. [32] and Umari et al. [12], respectively, as shown in the Supporting Information.

Starting from the Fermi golden rule, as shown in Eq. (2), Shuai et al. derived the equations for calculating the rate of the photophysical process [29,31], including the rate of fluorescence k_F, the rate of RISC k_{RISC}, the rate of internal conversion (IC) k_{IC}, and the rate of intersystem crossing (ISC) k_{ISC}. The i represents the initial state of $CH_3NH_3PbI_3$; f represents the final state; v represents the vibration in the initial state; v' represents the vibration in the final state; P is the Boltzmann distribution in Eq. (2). In Eq. (3), a and b are the vibration quantum numbers; c is the speed of light in a vacuum; Θ represents the vibration wave function; Q is the canonical coordinate of the nuclear motion; M_{if} is the transition dipole moment from the initial state i to the final state f, representing the electronic transition.

$$k = \frac{2\pi}{\hbar} \sum_{v,v'} P_{i,v} \left| H'_{iv,fv'} \right|^2 \delta\left(E_{f,v'} - E_{i,v}\right) \tag{2}$$

$$k_F = \frac{64\pi^4}{3hc^3} \left| M_{if}(0) \right|^2 \sum_a \sum_b v_{ib \to fa} \left| \int \Theta_{fa}(Q)^* \Theta_{ib}(Q) dQ \right|^2 \tag{3}$$

$$k_{RISC} = \frac{2\pi}{\hbar} \sum_v \sum_{v'} \left| \left\langle \phi_i \Theta_{i,v} \left| \hat{H}'_{SO} \right| \phi_f \Theta_{f,v'} \right\rangle \right|^2 \delta\left(E_{i,v} - E_{f,v'}\right) \tag{4}$$

$$k_{IC} = \frac{2\pi}{\hbar} \sum_{v,v'} P_{i,v} \left| \left\langle \phi_i \Theta_{f,v'} \left| \hat{H}_{BO} \right| \phi_f \Theta_{i,v} \right\rangle \right|^2 \delta\left(E_{f,v'} - E_{i,v}\right) \tag{5}$$

$$k_{ISC} = \frac{2\pi}{\hbar} \sum_{v,v'} P_{i,v} \left| \left\langle \phi_f \Theta_{fv'} \left| \hat{H}'_{SO} \right| \phi_i \Theta_{iv} \right\rangle \right|^2 \delta\left(E_{f,v'} - E_{i,v}\right) \tag{6}$$

The rate of RISC is sensitive to temperature [33]. k_{RISC} increases at high temperature, as shown in Eq. (7).

$$k_{RISC} \propto \exp\left(\frac{\Delta E_{st}}{k_B T}\right) \tag{7}$$

3. Results and discussion

For the photoluminescence measurements, $CH_3NH_3PbI_3$ was prepared on a quartz glass by solution route. The structure diagram of the device is shown in Fig. 2(a). The X-ray diffraction