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Review

Room-temperature phosphorescence from purely organic materials

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ABSTRACT

Room-temperature phosphorescence (RTP) materials have attracted great attention due to their involvement of excited triplet states and comparatively long decay lifetimes. In this short review, recent progress on enhancement of RTP from purely organic materials is summarized. According to the mechanism of phosphorescence emission, two principles are discussed to construct efficient RTP materials: one is promoting intersystem crossing (ISC) efficiency by using aromatic carbonyl, heavy-atom, or/and heterocycle/heteroatom containing compounds; the other is suppressing intramolecular motion and intermolecular collision which can quench excited triplet states, including embedding phosphors into polymers and packing them tightly in crystals. With aforementioned strategies, RTP from purely organic materials was achieved both in fluid and rigid media.

1. Introduction

In photophysics, phosphorescence arises from forbidden radiative transitions between the excited triplet state and ground state. Room-temperature phosphorescence (RTP) materials have attracted intensive interests due to their involvement of excited triplet states and comparatively long decay lifetimes. RTP materials have been applied in various fields, such as organic light-emitting diodes (OLEDs) [1], chemical and biological sensing [2], photovoltaic devices [3], bioimaging [4], and so on. In particular, RTP materials have a profound impact on the efficiency improvement of OLEDs, since they can utilize both triplet and singlet excitons generated during electrical injection and leading to a maximum internal quantum efficiency of 100%.

It has been extensively studied that some organometallic complexes, *i.e.* iridium complexes, are RTP materials owing to enhanced spin-orbit coupling induced by heavy atom effect. After a highly efficient non-doped OLEDs based on iridium complex has been fabricated [5], we mainly focused on improving device efficiency by designing efficient iridium complexes and optimizing device architecture [6]. Considering that noble metals present a large gap to commercialization, we have moved our interest to RTP materials with inexpensive, abundant and environmentally friendly properties, such as Cu(I) complexes [7] and purely organic materials.

Unlike organometallic complexes, most purely organic materials exhibited no RTP due to inefficient spin-orbit coupling and easy-quenched radiation relaxation process. Hence, the observation of phosphorescence from purely organic materials has been confined to cryogenic and inert conditions for a long time [8]. In 1977, Thomas et al. first reported that RTP could be observed inside micells after deoxygenation, which is known as micelle-stabilized RTP (MS-RTP) shortly afterwards [9]. Based on the initial report, cyclodextrin-induced RTP (CD-RTP) [10] and solid substrate-RTP (SS-RTP) [11] have been developed. In a protective ordered medium, excited triplet states of organic molecules are prone to radiative relaxation as non-radiactive relaxations are blocked by hindered molecular motions.

In this short review, recent progress on purely organic RTP materials is summarized after two basic principles for the phosphorescence emission have been analyzed. RTP were achieved both in fluid and rigid media from purely organic materials by promoting the ISC efficiency with specific compounds as well as suppressing non-radiative transition rates with phosphors confinement in polymers and crystals.

2. Basic principles for RTP

As shown in Fig. 1, the excited triplet state (T_1) is populated by ISC from excited singlet state (S_1), which is only possible through

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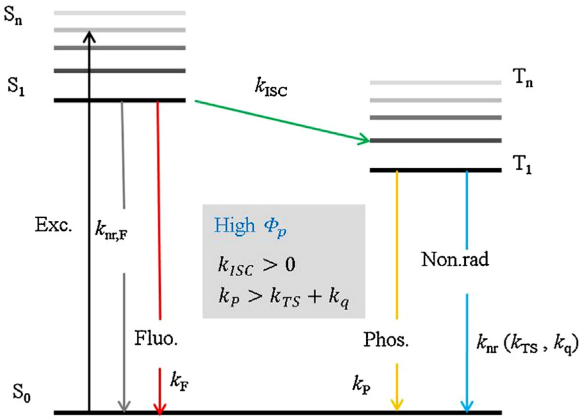


Fig. 1. A general Jablonski diagram of organic emitters is presented. Basic principles of RTP are shown in the grey box.

vibronic and spin–orbit coupling [12]. Thus, the first principle for phosphorescence observation is (i): $k_{ISC} > 0$, where k_{ISC} is the ISC rate. k_{ISC} is an intrinsic property of a molecule, which varies with the energy level and electronic configuration of the molecule. A small energy gap (ΔE_{ST}) between S_1 and T_1 levels facilitates ISC. It has been proved experimentally that when ΔE_{ST} is extremely small ($\leq$100 meV), both $S_1 \rightarrow T_1$ ISC and $T_1 \rightarrow S_1$ reverse ISC (RISC) are enhanced. In this case, triplet states become 'dark' and thermally activated delayed fluorescence (TADF) can be obtained [13]. As for electronic configuration, El-Sayed has shown that spin–orbit coupling can be greatly promoted by mixing singlet and triplet states of different electronic configurations, such as (π, π^*) and (n, π^*) [9]. Moreover, heavy atom effect (i.e. bromine or iodine atom) has been used externally and internally to increase $S_1 \rightarrow T_1$ conversion [14].

The second criterion for phosphorescence needs to be met (ii) $k_P > k_{nr}$, where k_P and k_{nr} are radiative and non-radiative transition rate from excited triplet state to ground state, respectively. Non-radiative channels can be divided into intramolecular losses (k_{TS}) and external losses caused by interaction with environment (k_q). At room temperature, the non-radiative loss, with rate of $k_{nr} \sim 10^2$–$10^6\ s^{-1}$, surpasses the radiative transition [12]. Consequently, suppression of non-radiative relaxation is perhaps the most significant and challenging part for efficient RTP from purely organic materials.

3. Achievement of RTP in fluid medium

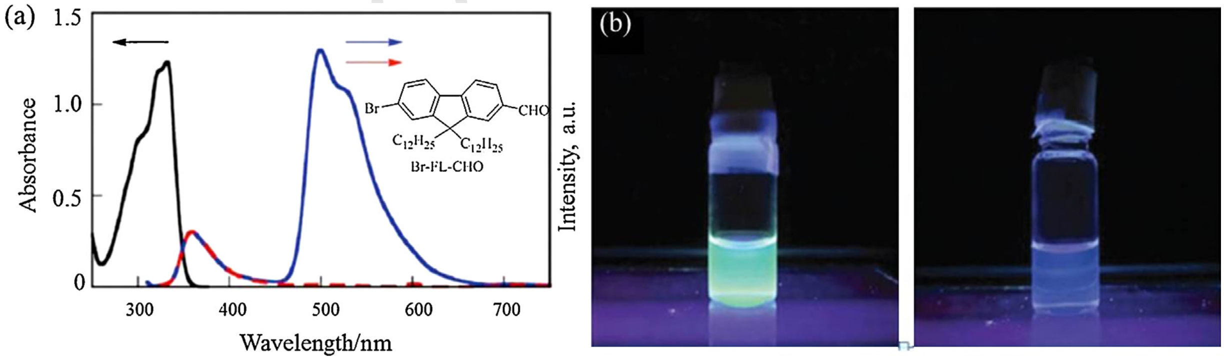
Based on aforementioned principles, RTP in fluid medium (*i.e.* solution), where intramolecular motion (rotation and vibration) and intermolecular collision are rampant and non-radiative relaxation is dominated, could be achieved mainly by promoting ISC efficiency. Non-bonding orbitals provided by a carbonyl or a heteroatom break the forbidden spin-orbit coupling between states of the same configuration in aromatic hydrocarbons. It is well known that $S \rightarrow T_{n,\pi}$ transitions in carbonyl compounds are much more probable (factor of 100–1000 times) than $S \rightarrow T_{\pi,\pi}$ in aromatic hydrocarbons [15]. Consequently, increasing ISC efficiency is feasible via introducing aromatic carbonyl, heterocycle, or heavy atom, and RTP in fluid medium could be realized when bringing two or three components to one molecule. However, RTP observed in solution was rare, since non-radiative transitions in a fluid medium are rampant.

By using both heavy-atom effect and nitrogen heterocycle, RTP was first confirmed in solution by Gutiérrez et al., which is beyond traditional rigid conditions for RTP observation [16]. Until in 2013, Takeuchi et al. reported that a fluorene derivative (Br-FL-CHO), which has both bromo and formyl groups, presented a bright RTP in a common organic solvent with phosphorescence quantum yield (φ_p) of 5.9%. The emission at 500 nm appeared under Argon (Ar) and completely disappeared in the presence of dioxygen, which is repeatable by bubbling Ar gas and exposure to air in turn (Fig. 2a). With a decay lifetime (τ) of 335 μs, the emission is unambiguously generated from excited triplet state. Further experiments indicated that RTP can be observed only when both bromo and formyl were existed in the fluorene parent. It comes to a conclusion that RTP in Br-FL-CHO is promoted by synergy of bromo and formyl substituents [17].

In 2014, Taddei et al. reported another class of RTP in solution based on 1,8-naphthalimide. Substituting a bromine atom at the 4-position enhances ISC through an internal heavy atom effect and prevents the generation of singlet charge transfer (^{1}CT) state due to a weak electron-withdrawing effect. With a further heterocycle substitution, the compound *N*-((pyridin-4-yl)methyl)-4-bromo-1, 8-naphthalimide (**2**) displayed a phosphorescent emission around 600 nm (τ = 332 μs) with φ_p of 0.59% in solution at room temperature (Fig. 3), which is different to the compound 4-bromo-1,8-naphthalimide (**1**), showing only fluorescence (Fig. 3a) [18].

4. Efficient RTP in rigid medium

Immobilizing molecules in a rigid medium is a promising way to prevent deactivation through intramolecular motion (i.e., rotation and vibration) and intermolecular collision, which leads to a suppression of non-radiative relaxation. By combination with promoted ISC efficiency, more and more RTP from purely organic materials was achieved in rigid media.



Q4 **Fig. 2.** (a) UV–vis (black line) and emission spectra of Br-FL-CHO (4.0×10^{-5} mol L^{-1}) under air (red dashed line) and Ar (blue line) in $CHCl_3$ at 298 K. Inset shows the chemical structure of Br-FL-CHO. (b) Images of Br-FL-CHO upon 365 nm excitation under Ar (left) and air (right) in $CHCl_3$ at 298 K. Adapted with permission from ref. [17]. Copyright 2013, Royal Society of Chemistry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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