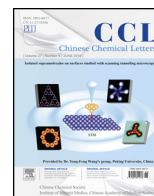




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Review

Crystallization-induced phosphorescence of pure organic luminogens

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ABSTRACT

This review summarizes the recent progress of efficient room temperature phosphorescence (RTP) from pure organic luminogens achieved by crystallization-induced phosphorescence (CIP), with focus on the advances in our group. Besides homocrystals, mixed crystals and cocrystals are also discussed. Meanwhile, intriguing RTP emission from the luminogens without conventional chromophores is demonstrated.

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1. Introduction

Luminescent materials with room temperature phosphorescence (RTP) have attracted increasing attention because of their fundamental importance [1] and wide applications in organic light-emitting diodes (OLEDs) [2], chemo- and bio-sensing [3], bioimaging [4], photodynamic therapy [5], and anti-counterfeiting techniques [6]. Distinguished from fluorogens [7], their longlived triplet excitons can exclude the interference from shortlived cellular autofluorescence background when used in bioimaging [4], and also can be potentially fully utilized in OLEDs. So far, RTP luminogens, however, are mainly inorganic and organometallic compounds with rare and expensive elements [8], such as rare earth metals, platinum, and iridium, although pure organic luminogens take intriguing advantages of low cost, relative ease of synthesis and processing, high stability, and facile functionalization. It is understandable that phosphorescence is generated by the occurrence of spin flip from lowest triplet excited (T_1) state to the ground (S_0) state, which is a quantum mechanically forbidden process. Without precious metals, the rate of phosphorescence is so slow that the longlived triplet excitons are inclined to undergo nonradiative decays through molecular motions (rotation and

vibration), collision processes, and interactions with quenchers like humidity and oxygen. Therefore, phosphorescence from pure organic luminogens is normally observed under cryogenic (e.g. 77 K) and inert conditions [9].

To diminish the nonradiative deactivations, different approaches, for instance, adsorption onto solid substrates or embedded into silica glasses, chelation, incorporation into polymer chains, and inclusion into surfactants or cyclodextrins have been developed to realize RTP [10]. In most cases, however, merely inefficient phosphorescence is obtained. In 2010, Tang and coworkers observed a unique phenomenon of crystallization-induced phosphorescence (CIP) in a series of pure organic luminogens, such as benzophenone (BP), methyl 4-bromobenzoate (MBB), and 4,4'-dibromobiphenyl (DBBP') [11]. Namely, these luminogens are nonphosphorescent (some even virtually nonemissive) in solution and amorphous states, however, they demonstrate efficient RTP upon crystallization [11]. The discovery of CIP phenomenon opens up a crystal engineering approach to achieve efficient RTP from pure organic luminogens. It is found that restriction of intramolecular motions (RIM) is mainly accountable for the CIP phenomenon, which is analogous to the mechanism of aggregation-induced emission (AIE) [12]. Meanwhile, effective isolation from oxygen and moisture via the self-protective crystal lattice further promotes the RTP emission. Later, similar phenomenon was reported by Kim and coworkers [3]. Subsequently, on the basis of fundamental considerations of carbonyl groups, heteroatoms, and heavy atom effect [1a,14], efficient RTP from pure organic luminogens was received through

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further (co)crystallization, doping/trapping in rigid matrices, creating intermolecular interactions between luminogens and hosts, and even singlet fission [15–28]. In this review, we focus on the recent progress of CIP luminogens, aiming to show a brief picture on this exciting renewed area.

2. CIP of benzophenones and benzils

It is well known that BP is phosphorescent at cryogenic temperatures, whose intersystem crossing (ISC) efficiency is approaching unity. In 2010, Tang and coworkers discovered the unique CIP phenomenon of BP [11]. BP molecules exhibit merely negligible fluorescence in neither protic nor aprotic solvents, or amorphous states when absorbed onto thin-layer chromatography (TLC) plates or incorporated into polymethyl methacrylate (PMMA) films under ambient conditions, while being highly phosphorescent upon crystallization, with solution and crystal efficiencies (Φ_s and Φ_c) of 0.001% and 15.9%, respectively. Similar phenomenon is observed in its derivatives (DFBP, DCBP, DBBP, BBP, and ABP), MBB, as well as DBBP' (Fig. 1), with phosphorescence efficiency (Φ_p) up to 40%. The nonluminescence of these compounds in solution and amorphous states is ascribed to the collisions and/or active intramolecular motions, which can effectively annihilate the exciton energies via nonradiative relaxations even in rigid polymer films. When cooled to 77 K, however, the solutions, polymer films, and spots on TLC plates all exhibit strong phosphorescence, indicative of the crucial role of structure rigidification (Fig. 1c). Notably, the spot of DFBP dotted on a TLC plate with six times forms a crystalline outer rim that is emissive at room temperature.

Based on above results, it is rational to speculate that some special interactions in the crystalline state have helped to restrict intramolecular motions of the molecules, thus generating rigidified molecular conformations and turning on the RTP emission. Further scrutinization of their crystals confirms it. As exemplified in Fig. 1d, abundant C–H...O (2.724, 2.777 Å) and C–H...F (2.796 Å) hydrogen bonds are present in the DFBP crystals, which seriously lock the molecular conformations and restrict the molecular motions. Crystal structures of the other compounds show similar multiple intermolecular interactions, like C–H...O, C–H...X (X = F, Cl, Br),

N–H...O, C–H... π hydrogen bonds, and C–Br...Br–C halogen bonds. The structural rigidification effect induced by such intermolecular interactions activates the RIM process and makes the molecules highly phosphorescent in the crystalline state at room temperature. In addition, those crystalline lattices can also protect the luminogens away from quenching substances as oxygen and moisture, thus further enhancing the phosphorescence emission.

Generally, carbonyl group and nonplanar conformations are favorable for effective spin-orbit coupling, thus facilitating the ISC processes from lowest excited singlet (S_1) state to T_1 state and enhancing the probability of phosphorescence emission. Compared to BP, benzil (BZL) contains one more carbonyl group and even more twisted conformations. Therefore, it is expected BZL is also CIP-active. Exactly, dissolving it in varying oxygen-free organic solvents or dotting it on TLC plates, there is no visible emission; upon crystallization, however, intense green phosphorescence (521 nm) with the lifetime ($\langle\tau\rangle$) of 142 μ s is observed (Fig. 2) [17]. Fig. 2e illustrates the fragmental molecular packing arrangement of BZL in the crystal. Clearly, numbers of nonclassic C–H...O hydrogen bonds (2.416, 2.417, 2.482, 2.483 Å) between one molecule and six adjacent cousins form a 3D interactions network, which tightly fixes the benzene rings and carbonyl groups, thus stiffening the molecular conformations and diminishing the exciton energy dissipations through molecular motions and collisions. What's more, the highly twisted conformations of BZL also prevent the formation of detrimental species such as excimers or exciplexes in the crystalline state, thus offering bright RTP.

Besides BZL, its derivatives like DFBZL, DBBZL, DMeBZL, DMeOBZL, and BBZL (Fig. 2a) also demonstrate typical CIP characteristics, with RTP maxima at 500, 526, 505, 517, and 584 nm, respectively. The significantly red-shifted emission of BBZL is ascribed to its extended conjugation, and moreover greatly enhanced spin-orbit coupling and lowered energy difference between T_1 and S_0 states.

3. Crystallization-induced dual emission (CIDE) from aromatic acids and esters

Above results suggest that carbonyl group and effective intermolecular interactions are favorable for RTP emission at

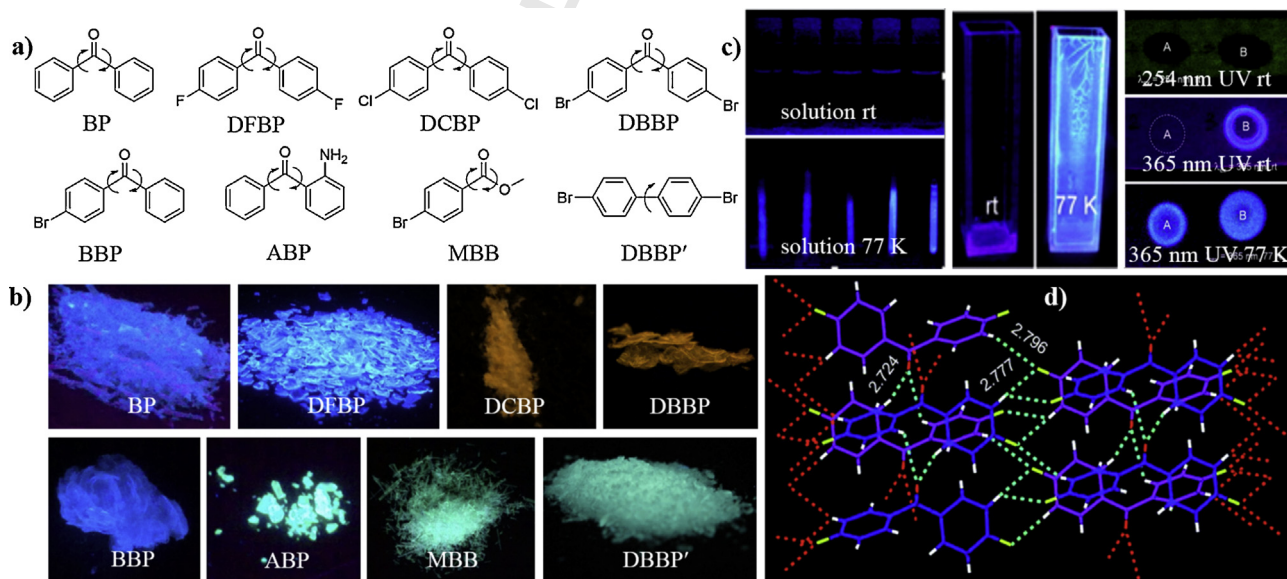


Fig. 1. (a) Chemical structures and (b) photographs of luminescent crystals for BP and its derivatives, MBB, and DBBP'. (c) Photographs of DFBP in solutions [from left to right: *n*-hexane, tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile, ethanol] and PMMA films, and on a TLC plate at room temperature and 77 K taken under UV irradiation. (d) Perspective view of molecular packing arrangement and intermolecular interactions in DFBP crystals. Reproduced with permission from Ref. [11].

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