

Room temperature phosphorescence from natural products: Crystallization matters

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Efficient room temperature phosphorescence is observed in natural compounds and polymers such as starch, cellulose, bovine serum albumin (BSA), and some other carbohydrates. Whereas being practically nonluminescent in solutions and TLC plates, they emit bright phosphorescence in the crystalline states with lifetime up to microseconds, exhibiting crystallization-induced phosphorescence (CIP) characteristics. The CIP of these natural products without any conventional chromophores offers a new platform for the exploration of conceptually novel luminogens.

room temperature phosphorescence, natural products, cellulose, starch, bovine serum albumin

1 Introduction

The essential differences between fluorescence and phosphorescence are the degeneracy of the excited states, the far longer lifetimes of triplets versus singlets, and the sensitivities of triplets to a wider variety of quenching conditions. Such differences endow phosphorescent materials unique photophysical properties and advantages in a number of potential applications, for examples, organic light emitting diodes [1, 2], photovoltaic devices [3, 4], sensors [5, 6] and bioimaging [7, 8]. However, so far phosphorescent luminogens are essentially inorganic and organometallic compounds because metals could promote spin-orbit coupling. Normally, these materials require rare and expensive elements such as rare earth metals, platinum and iridium. Pure organic luminogens might be better choices because of their wider availability and better tailorability. However, it is

difficult to obtain efficient room temperature phosphorescence (RTP) from pure organic molecules due to the spin-forbidden of triplet exciton transition, thermal deactivation and chemical quenching during the long lifetime of triplets. Although solid substrate RTP (SSRTP) [9], micelle stabilized RTP (MS RTP) [10], cyclodextrin-induced RTP (CD-RTP) [11] have been reported, their efficiencies are rather low, most of which are only at detectable levels.

Despite the importance of phosphorescent materials, it is still challenging to obtain efficient pure organic RTP luminophores. In 2010, we discovered a new phenomenon of crystallization-induced phosphorescence (CIP) in the crystals of benzophenone and its derivatives at room temperature, whose phosphorescence quantum yield was up to 40% [12]. While these luminogens are practically nonphosphorescent in solutions and amorphous solid state, they emit bright phosphorescence in the crystal state. The mechanism for CIP phenomenon was proposed to be associated with the restriction of intramolecular rotations due to the effective intermolecular interactions in the crystals. Later, Kim [13],

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Jin [14] and Yong [15] *et al.* reported similar RTP phenomena in their systems.

We are interested in the further exploration of new RTP luminogens. In this paper, we report our recent discovery on RTP from crystalline natural products, for instance, rice, starch, cellulose, and bovine serum albumin (BSA). Their photophysical properties in solutions, TLC plates and crystalline state were compared and briefly discussed. This is the first example of study on CIP behaviors of natural products. Some of them are highly emissive although they contain no any conventional chromophores. We believe the exploration of these systems will offer us with new insights into the photophysical processes of organic luminogens.

2 Results and discussion

2.1 CIP of the rice

Under 365-nm UV light illumination, rice emits a bright blue light with a peak and a shoulder at 382 and 433 nm (Figure 1, panels (a) and (b)), at which both short and long lifetimes $\langle\tau\rangle$ of 1.72 ns/2.91 μ s and 1.78 ns/5.26 μ s were detected, respectively (Figures 1(c) and S1), indicating dual fluorescence and phosphorescence emissions from the rice. It is amazing that rice can emit efficient blue phosphorescence at room temperature as RTP is hardly observed in pure organic compounds. Moreover, the biocompatible and environmentally benign features of rice make it attractive in emerging luminescence technologies. Our previous work implies that intermolecular interactions are effective to decrease the vibrational dissipations of the excitons and therefore helpful for the light emission [12, 16, 17]. For rice, there should be such strong intermolecular interactions as hydrogen bonds owing to the presence of many oxygen and hydroxyl groups. X-ray diffraction (XRD) measurement gives sharp peaks at 2θ of 15.2, 17.3, 18.2 and 20.3° in the diffractogram pattern (Figure 1(d)), which suggests the crystalline nature of rice. Such crystalline structure further fixes the conformations of the luminogens, thus decreasing thermal deactivations and promoting the light emissions.

2.2 CIP of starch, cellulose and BSA

The blue emission of rice prompted us to explore why it is luminescent and what has activated its phosphorescence process. It is known that the major component of rice is starch. We thus checked whether starch was luminescent. When an aqueous solution of starch (0.1 mg/mL, Figure 2(a)) was placed under 365-nm UV illumination, no emission was observed (Figure 2(b)). When the solution was dropped onto a thin layer chromatography (TLC) plate, it was still nonluminescent. However, when the solution was cooled to 77 K by liquid nitrogen, it emitted a blue light under UV excitation (Figure 2(c)). This result indicates that starch undergoes active nonradiative transitions in the solu-

tion and TLC plate, which are greatly impeded in the solid glassy state. Starch powder emission was also checked. Interestingly, it emitted brightly even at room temperature (Figure 3(a)). Together with the above results, it is assumed that crystallization helps to prevent thermal dissipations and promotes the powder emission because starch is naturally crystalline as powders.

Starch is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds, which is similar to that of cellulose. The natural question here is thus whether cellulose is also luminescent at room temperature? Further tests revealed the similar emission behaviors of cellulose to those of starch in the solution and solid states (Figure 2 and Figure 3(b)). Such fascinating emission behaviors of natural starch and cellulose inspired us to check whether other natural macromolecules are also luminescent. We turned our attention to proteins, which widely exist in plants, animal and human bodies. BSA, an often used protein for experimental research, was chosen as an example. Strikingly, BSA is practically nonluminescent in solvents and TLC plates, but its aqueous solution becomes highly emissive at cryogenic temperature (Figure 2). Moreover, similar to what have observed for starch and cellulose, BSA solid powders exhibited bright blue emission upon UV light excitation (Figure 3(c)).

To collect more information about emission behaviors of these natural products, the photoluminescence spectra of their aqueous solutions (spectrum of cellulose not shown due to the interference from urea [18]) and solid powders were measured. Whereas starch and BSA give emission peaks at ~332/370 and 340 nm, the solid powders of starch, cellulose, and BSA depict broad emission spectra with peak maxima at 470, 427, and 418 nm (Figure 4(a)), respectively. In comparison to the solution emissions, the solid powder emissions are not only greatly enhanced but also largely red-shifted (up to >100 nm). Similar to the rice emission, both fluorescence and phosphorescence were detected in the solid powders of starch, cellulose, and BSA, whose $\langle\tau\rangle$ values are 12.83 ns/4.98 μ s, 2.39 ns/4.66 μ s and 3.63 ns/4.75 μ s, respectively, (Figures 4(b) and S2). Further XRD measurement show diffraction peaks at 2θ values of 14.5/17.1/19.6/22.4, 15.3/22.5/34.4 and 9.5/20.0° for the solid powders of starch, cellulose, and BSA (Figure 4(c)), respectively, revealing that the powders are crystalline in nature.

2.3 CIP mechanism of the natural products

It becomes clear that starch, cellulose and BSA are practically nonluminescent in solution and amorphous states (in TLC plates) but become highly phosphorescent in crystalline state at room temperature. These behaviors testify our previous assumption that crystallization is helpful for the starch emission. Such CIP characteristics of the natural polymers are similar to those observed in the benzophenone

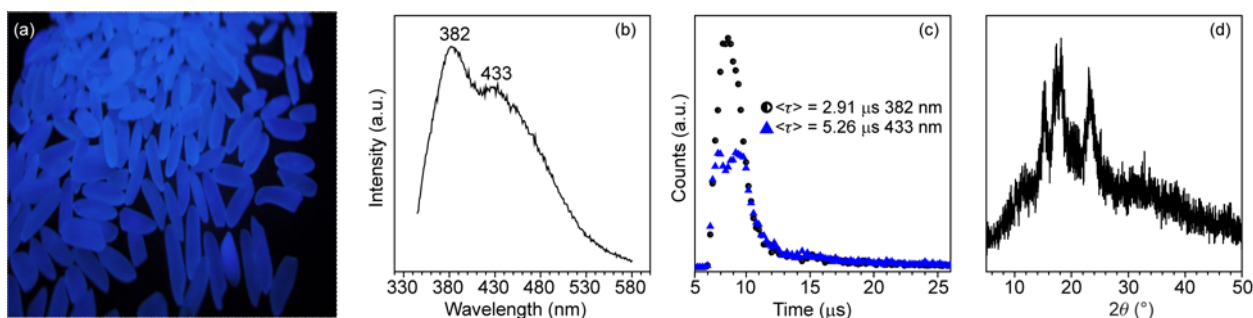


Figure 1 (a) Photograph of the rice taken under 365-nm UV light illumination; (b) emission spectrum; (c) time-resolved emission decay profiles and (d) XRD pattern of the rice. Excitation wavelength = 300 nm. The curves in (c) are monitored by a phosphorescence lifetime detector.



Figure 2 Photographs of the solutions of starch (left), cellulose (middle) and BSA (right) taken at room temperature (a, b) and 77 K (c) under room lighting (a) and 365-nm UV illumination (b, c).

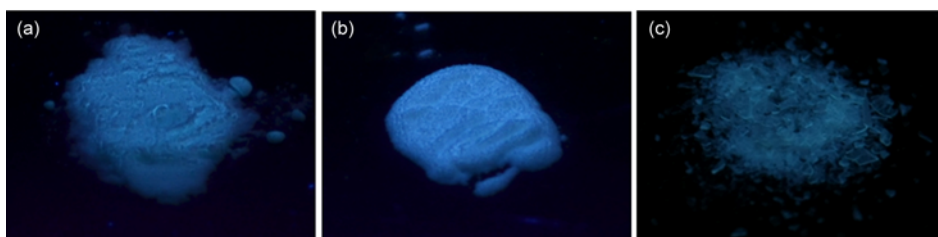


Figure 3 Photographs of the solid powders of starch (a), cellulose (b) and BSA (c) taken under 365-nm UV illumination at room temperature.

systems [12]. The nonradiative deactivation pathways of triplet excitons are active and dominant in the solution and amorphous states at room temperature, thus giving faint emissions. However, upon crystallization, due to strong and abundant intra- and intermolecular interactions, the molecular conformations of these natural polymers are rigidified. Subsequently, the vibrational dissipations are blocked, thus giving enhanced emissions.

Although it is understandable that crystallization is in favor of the emissions for these natural products, more fundamental issues must be addressed. Except for BSA, in which amino acids can act as luminogenic units, neither starch nor cellulose contains any conventional chromophores, what is (are) the basic emissive unit(s) for them? Electron-rich oxygen and/or glucose units are accountable for the unique emission behaviors. Although there is no classic chromophore, there are numerous electron-rich oxygen-containing groups with lone pair electrons. In the solid crystalline powders, through proper contacts, such groups may form a variety of clusters, in which electron clouds of

the oxygen groups are overlapped and shared, thus generating novel clustered electron-rich chromophores with lowered energy gaps and extended effective conjugation lengths. Meanwhile, effective molecular interactions significantly prevent nonradiative deactivation channels, thereby endowing such “clustered chromophores” highly emissive in the solid powder states.

In our laboratories, we have also found that chitosan, dextran, glycogen, glucose, xylose, and galactose (Chart 1) exhibit CIP phenomena, thus further supporting our above proposed mechanism. Further study of these systems and their derivatives may help us reveal the detailed involved electronic interactions among the molecules and explore more efficient new phosphor systems without conventional chromophores.

3 Conclusion

In summary, we have for the first time demonstrated the

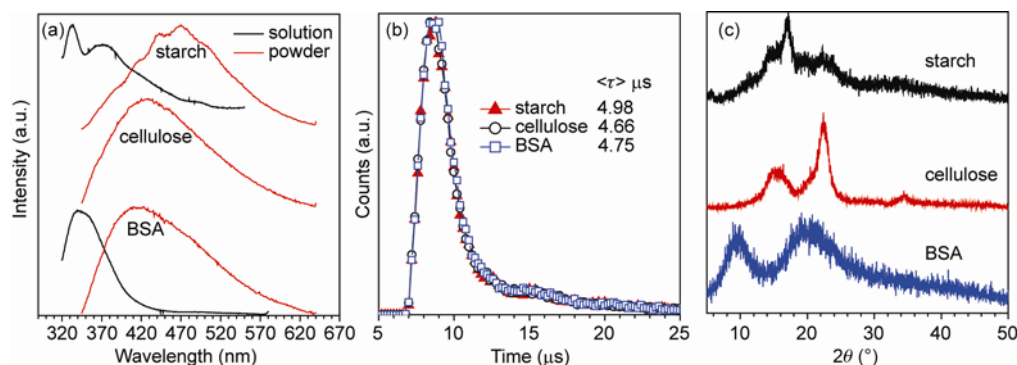


Figure 4 Solution and powder emissions (a), phosphorescence decay curves (b) and powder XRD curves (c) of starch, cellulose and BSA at room temperature.

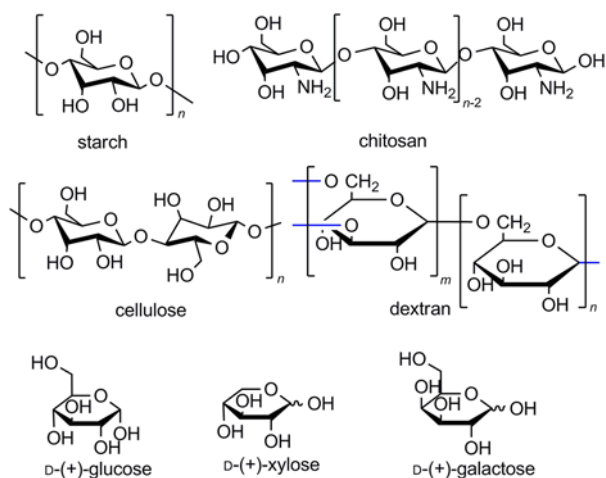


Chart 1 Structures of some pure organic nonconventional luminogens with CIP characteristics at room temperature.

CIP behaviors of natural products such as starch, cellulose, and protein without any conventional chromospheres at room temperature. Novel nonconventional chromophores consisting of a variety of clustered electron-rich groups with lone pair electrons are responsible for the efficient phosphorescence in the crystalline solid powders. This discovery is of crucial importance to explore more RTP luminogens and nonconventional chromophores. It also offers new mechanistic insights into the underlying causes of autofluorescence from biological systems. Due to their biocompatibility, optical activity, environmental benignity, etc., these emissive natural products may be widely used in bioimaging, sensing, circularly polarized emission-based optoelectronic devices, and so on. The photophysical processes and potential applications of these natural compounds will be thoroughly studied and reported in due course.

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