

Room-Temperature Phosphorescence of Natural Silkworm Cocoon Silk

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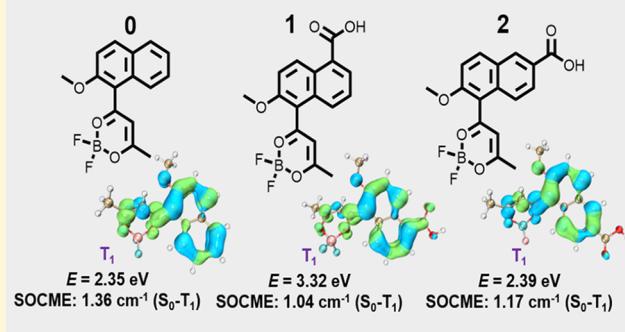
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ABSTRACT: Due to its advantages, such as biocompatibility and controllability, silk has been used in various biomedical applications. Nowadays, researchers have improved silk fibers with new functions to expand their applicability. Many studies have focused on improving leaves feeding for silkworms to produce fluorescence, and the study of organic afterglow silkworm cocoon silk (SCS) is an unprecedented innovative combination. Here, we use natural SCS to prepare room-temperature phosphorescent materials by doping with luminescent difluoroboron β -diketonate (BF_2bdk). SCS shells can provide a rigid environment for the BF_2bdk triplet to suppress its nonradiative decay and oxygen quenching. In addition, room-temperature phosphorescent materials were prepared by improving leaves and processing raw silk as well as using natural products such as feathers and shells as matrices. There is a lot of potential application value of widely sourced, diverse in composition, environmentally friendly, and sustainable natural functionalized products.



Natural protein fiber materials have been attracting the curiosity of scientists for many years due to their superior biocompatibility and biodegradability.^{1–3} Among them, silk from silkworm cocoons is considered as a natural polymer composite material, consisting of two core silk filaments bonded by a gelatinous silk gum layer with a length of about 1000 m and a diameter of 10–30 μm and is well-known for its applications in the textile industry.^{4–6} For many years, silkworm cocoon silk has been used in the biomedical field, including tissue engineering, drug delivery systems, biomedical implants, and medical devices.^{7–9} In addition, functional fluorescent silk has been found to have promising optical and photonics applications.¹⁰ Functional fluorescent silk has been prepared by incorporating quantum dots,^{11–13} grafting organic dyes onto silk,^{14,15} and so on. However, there have been no reports of organic room-temperature phosphorescence from silkworm cocoon silk.

Room-temperature phosphorescence (RTP) and organic persistent luminescent materials have attracted significant research interest due to their long-lived excited-state properties and potential applications in optical sensing, bioimaging, and data encryption.^{16–24} In most organic persistent luminescence systems, the long-lived excited state originates from the triplet excited state.^{25–28} It is well-known that intersystem crossing (ISC) is spin-forbidden in organic systems, and nonradiative decay and oxygen quenching compete significantly with

phosphorescent decay.^{29,30} Therefore, achieving efficient organic phosphorescent materials under ambient conditions is not an easy task. To address this issue, researchers in the field have developed material fabrication strategies such as the heavy-atom effect and $n-\pi^*$ transition, controlling molecular aggregation, and defining explicit supramolecular assembly to enhance intersystem crossing and phosphorescent decay and reduce nonradiative decay and oxygen quenching of organic triplets, significantly improving the efficiency and lifetime of organic persistent luminescence.^{31–44}

Furthermore, the two-component design strategy developed by us and other researchers has demonstrated significant capabilities in enhancing the performance of organic RTP and persistent luminescence.^{45–54} In this strategy, the use of an organic matrix (second component) to control the excited-state properties of the luminescent dopant (first component) has shown strong potential in constructing high-performance organic persistent luminescent materials.^{43,51,52,55–58} For example, crystal or glass matrices have been used in dopant-

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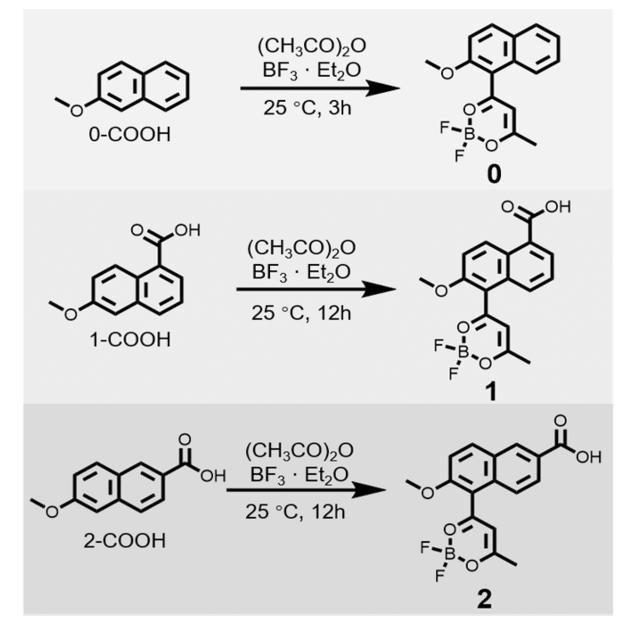
matrix systems to suppress the nonradiative deactivation and oxygen quenching of the luminescent dopant's triplet excited state, leading to the preparation of efficient organic RTP and persistent luminescent materials.^{59,60}

The two-component design strategy allows for the flexible selection of organic components and the use of simple synthetic methods to prepare organic RTP and persistent luminescent materials, which is a clear advantage of this approach.^{61–64} We reason that natural silkworm cocoon silk (SCS) can be used as a matrix to prepare natural, room-temperature, persistent luminescent materials. There would be two methods for the preparation: (1) direct processing on functionalized natural silkworm cocoon silk and (2) improving silkworm feed with leaves containing phosphorescent molecules.^{65–67}

The luminescent difluoroboron β -diketonate compounds (BF_2bdk) with intramolecular charge transfer emission characteristics were selected as the phosphorescent dopant.^{28,29,55,58} Due to its high Φ_{ISC} in the naphthalene system, based on our previous research, the BF_2bdk compounds in this study were designed to contain a naphthalene group for the preparation of room-temperature persistent luminescent materials with a strong propensity for ISC. Simultaneously, natural silkworm cocoon silk, raw silk, and other natural rigid materials (such as feathers, shells) were also used as matrices to prepare natural room-temperature persistent luminescent materials, which holds innovative significance.

Scheme 1 describes the synthesis of BF_2bdk compounds **0**–**3** via cascade reactions using aromatic substrates, acetic

Scheme 1. Cascade Synthesis of BF_2bdk Compounds **0, **1**, and **2****



anhydride, and boron trifluoride diethyl etherate. The synthesis method, structural characterization of FTIR, LRMS, HRMS, ^1H NMR, ^{13}C NMR, ^{11}B NMR, ^{19}F NMR (Figures S23–S43), and purity information on HPLC (Figure S16) are provided in the Supporting Information, demonstrating successful synthesis. Single crystal analysis further confirmed the molecular structure (Figure S44).

The UV-vis absorption spectra of compound **0** in dichloromethane display a low-energy absorption band between 360 and 420 nm, with a maximum absorption band at 388 nm, attributed to the intramolecular charge transfer (ICT) transition from the aromatic donor to the dioxaborine acceptor (Figure S1 and Table S1, Supporting Information). Compounds **1** and **2** in dichloromethane solution both exhibit a slight ICT blue shift in the UV-vis spectra, with maximum absorption bands at 377 and 379 nm, respectively (Figure S1). TD-DFT calculations show that, in these BF_2bdk systems, the oscillator strength of the $S_0\text{-}S_1$ ICT transition is relatively small, which aligns well with the experimentally observed weaker UV-vis absorption (Figure 1A). These small $S_0\text{-}S_1$ oscillator strengths can lead to a small fluorescence rate (k_F), which is a prerequisite for high Φ_{ISC} . The steady-state emission spectra of compound **0** in acetone (ACE), dichloromethane (DCM), ethyl acetate (EA), and tetrahydrofuran (THF) solutions (excited at 365 nm) showed fluorescence bands ranging from 450 to 550 nm, with maximum values at 494, 494, 468, and 468 nm, respectively (Figure S2). Compounds **1** and **2** in dichloromethane solution exhibit maximum emission bands at 470 and 464 nm, respectively. Additionally, the solid and solution forms of the single-component BF_2bdk compounds show no persistent luminescence at room temperature upon UV excitation (Figure S3).

Our recent research, along with that of others, has indicated that, in two-component persistent luminescent systems, an appropriate organic matrix contributes to the ISC of the luminescent dopant and protects the dopant's triplet excited state from nonradiative decay and oxygen quenching (Figure 1B).^{55,61–63} Natural silkworm cocoon silk as a semicrystalline matrix can protect the triplet state of the dopant in a rigid environment at room temperature. A small piece of natural silkworm cocoon silk shells was taken and soaked in BF_2bdk -ACE solutions of different concentrations for 2 h to prepare two-component materials (Figure 2A). After drying, the **0**-SCS at 1% concentration, as well as **1**-SCS and **2**-SCS at 0.5% concentration, exhibited the longest persistent luminescence and phosphorescence lifetimes (Figures S4–S6). When phenyl benzoate (PhB) was used as an organic matrix, it was found that BF_2bdk -PhB also exhibited good organic persistent luminescence (Figures S7–S9). These observations indicate that a rigid matrix can restrict the intramolecular motion of excited-state molecules and significantly suppress the nonradiative decay of the triplet excited state. BF_2bdk -SCS exhibits room-temperature afterglow, and their photophysical study has been conducted (Figure 2B–D). In steady-state emission spectra of the **0**-SCS-1% material, it was found that the emission band was between 400 and 550 nm, with a maximum emission at 455 nm (Figure 2E). Its delayed emission spectra (with a delay of about 1 ms) were in the range of 450–600 nm, with a maximum emission at 523 nm, and a phosphorescence lifetime of 151.8 ms with a photoluminescence quantum yield (PLQY) of 3.09% (Figure 2F). Also, the steady-state emission spectra of the **1**-SCS-0.5% and **2**-SCS-0.5% materials had maximum peaks at 459 and 442 nm, respectively, and their delayed emission spectra peaks were at 533 and 525 nm (Figure 2G,I). Phosphorescence lifetimes were 260.0 and 265.2 ms with 3.12 and 3.21% PLQY, respectively (Figure 2H,J). Additionally, it was found that these samples could be excited by 405 nm light (Figure S10). TD-DFT calculations (Figures S11–S13) revealed that the T_1 state's electron–hole isosurface maps of the BF_2bdk compounds were very similar,

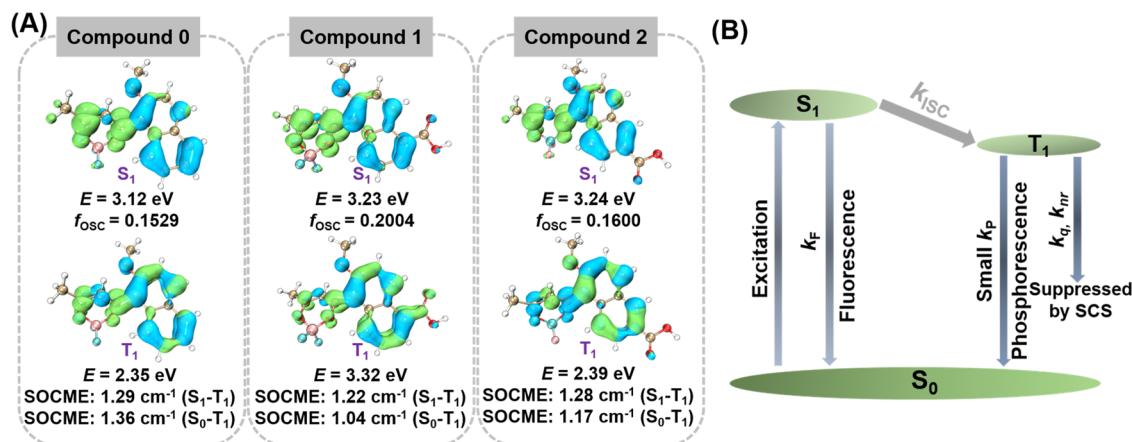


Figure 1. (A) Isosurface maps of electron–hole density difference of the singlet and triplet excited states of compounds 0, 1, and 2, where blue and green isosurfaces correspond to hole and electron distributions, respectively, and spin–orbit coupling matrix element (SOCME) values. (B) Proposed RTP mechanism of BF_2bddk -SCS material.

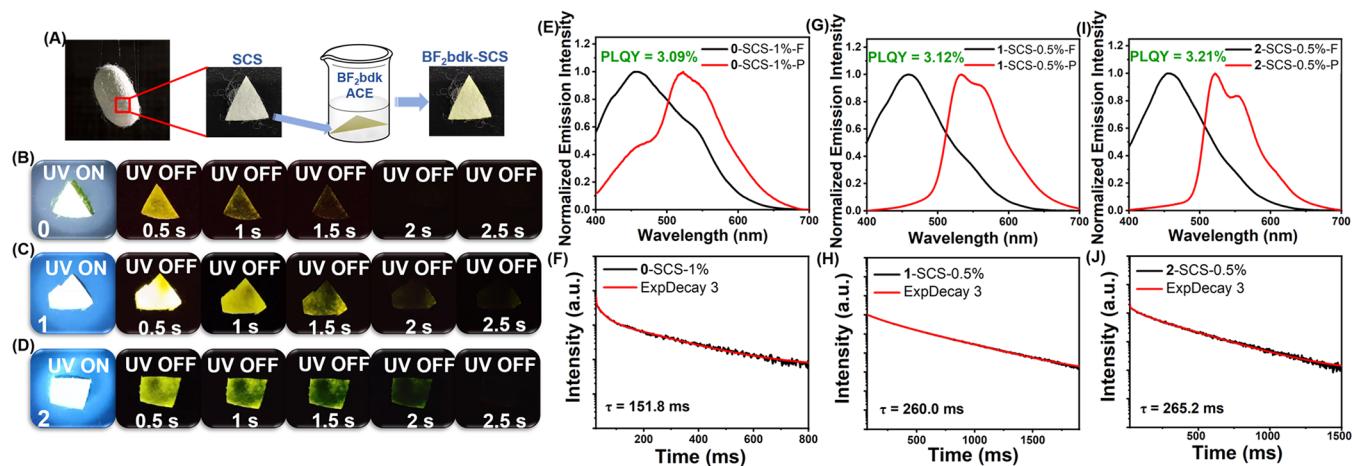


Figure 2. (A) The preparation process of BF_2bddk -SCS. Photographs of (B) 0-SCS-1%, (C) 1-SCS-0.5%, and (D) 2-SCS-0.5% materials under UV lamp and after ceasing the UV lamp. Room-temperature steady-state and delayed emission spectra of (E) 0-SCS-1%, (G) 1-SCS-0.5%, and (I) 2-SCS-0.5% materials (in air). Room-temperature phosphorescence decay of (F) 0-SCS-1%, (H) 1-SCS-0.5%, and (J) 2-SCS-0.5% materials (in air).

showing a local excitation (LE) and an ICT characteristic, reflecting their long-lived RTP properties. Compared with other natural-based afterglow materials, it also has longer phosphorescence lifetimes (Table S2).

To confirm that BF_2bddk exhibits an RTP-type luminescence mechanism, energy transfer, donor–acceptor luminescence, and impurity-induced mechanisms have been definitively ruled out, all of which have the potential to induce luminescence. (1) Room-temperature phosphorescence can be induced by excited-state energy transfer from the RTP donor to the emitting acceptor, and the energy transfer process only occurs when the donor is sufficiently excited.^{41,42} However, the obtained BF_2bddk -SCS material in this study can be excited by 365 nm UV light (Figure S14), and the SCS matrix shows negligible UV-vis absorption at 365 nm (Figure S15). Therefore, the possibility of room-temperature phosphorescence induced by energy transfer from the SCS matrix to BF_2bddk can be ruled out. (2) Recent research suggests that when the T_1 level of the organic matrix falls between the S_1 and T_1 states of the dopant, the T_1 state of the organic matrix can facilitate the ISC of the dopant from singlet to triplet, leading to organic room-temperature phosphorescence.³⁵ However,

this ISC-mediated process does not apply to the BF_2bddk -SCS system in this study, as the T_1 level of the SCS matrix is significantly higher than those of the S_1 and T_1 states of the BF_2bddk molecule. Moreover, the high T_1 level of the organic matrix plays a vital role in preventing luminescence quenching caused by triplet–triplet energy transfer from the luminescent dopant to the organic matrix, enabling the construction of high-performance luminescent materials.⁶⁴ (3) In organic materials, the donor–acceptor mechanism can generate charge separation states, and the long-lived luminescence observed in organic systems is attributed to delayed charge recombination in rigid solid matrices.¹⁷ For organic donor–acceptor luminescent systems, the formation of charge-separated states through intermolecular charge transfer between donor and acceptor molecules is necessary for persistent luminescence. However, negligible intermolecular charge transfer between the BF_2bddk dopant and the organic matrix was observed in this study due to the lower HOMO and higher LUMO levels of the latter, excluding the possibility of a long-lasting luminescence mechanism in this system. (4) BF_2bddk has been purified by column chromatography and confirmed to be of high purity through HPLC (Figure S16).⁶⁸ The UV-vis absorption

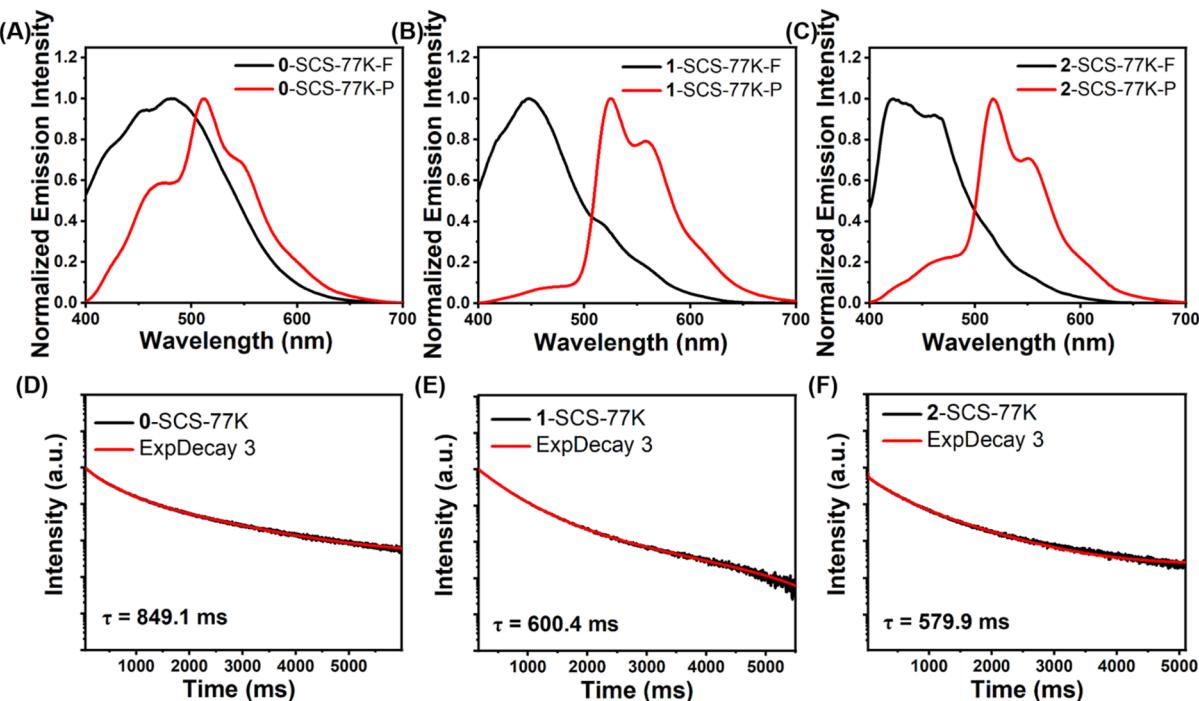


Figure 3. Steady-state and delayed emission spectra of (A) 0-SCS, (B) 1-SCS, and (C) 2-SCS materials at 77 K. The phosphorescence decay of (D) 0-SCS, (E) 1-SCS, and (F) 2-SCS materials at 77 K.

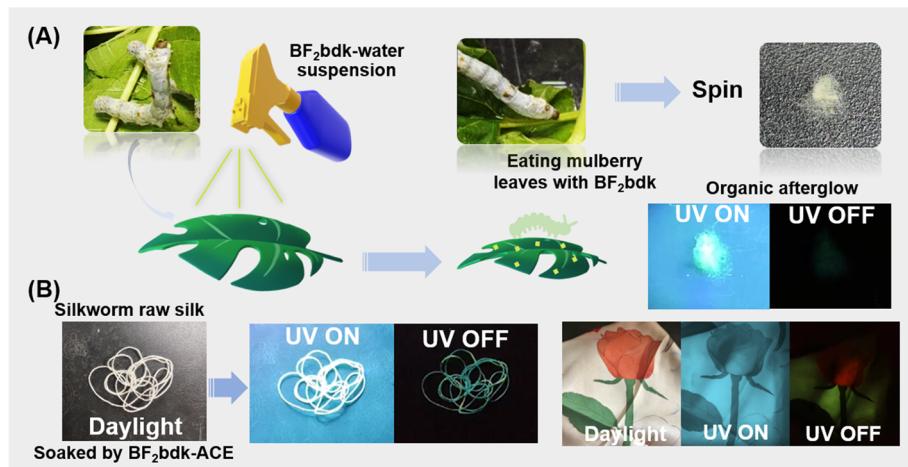


Figure 4. (A) Feeding silkworms with leaves containing BF_2bddk . (B) Silk thread containing BF_2bddk with RTP characteristics and emitting afterglow silk.

spectra exhibit the electronic absorption characteristics of the BF_2bddk dopant, while the excitation spectra show the absorption characteristics of the luminescent component. The matching between the UV-vis absorption spectra and the excitation spectra indicates that the fluorescence properties originate from the BF_2bddk dopant rather than impurities. Based on the above experiments and analysis, we propose (Figure 1B) that, under excitation, the singlet excited state of BF_2bddk is formed and then undergoes effective ISC to reach the triplet excited state, resulting in the occurrence of organic room-temperature afterglow.

Delayed emission spectra and decay at 77 K show that phosphorescence lifetime increases at low temperature, which is a typical behavior of the phosphorescence mechanism. In the steady-state emission spectrum, 0-SCS exhibited a peak at around 481 nm, and the delayed emission spectrum (1 ms

delay) was at 512 nm with a phosphorescence lifetime of 849.1 ms, which is significantly longer than that at room temperature (Figure 3). Also, the phosphorescence lifetimes of 1-SCS and 2-SCS at 77 K are 600.4 and 579.9 ms, respectively. Additionally, SCS is a natural macromolecular polymer matrix, and according to previous studies, polar polymer matrices can simultaneously reduce the k_F of the ICT state and increase the k_{ISC} of the ICT state through dipole-dipole interactions, significantly promoting the ISC of the excited state of BF_2bddk . Furthermore, the rigid microenvironment provided by the polymer matrix can restrict the nonradiative deactivation of the triplet state of BF_2bddk and to some extent protect the triplet state from oxygen quenching.⁶⁹ According to previous research, the organic afterglow characteristics of polymer-based materials typically cannot be activated through short-term and low-power excitation under environmental con-

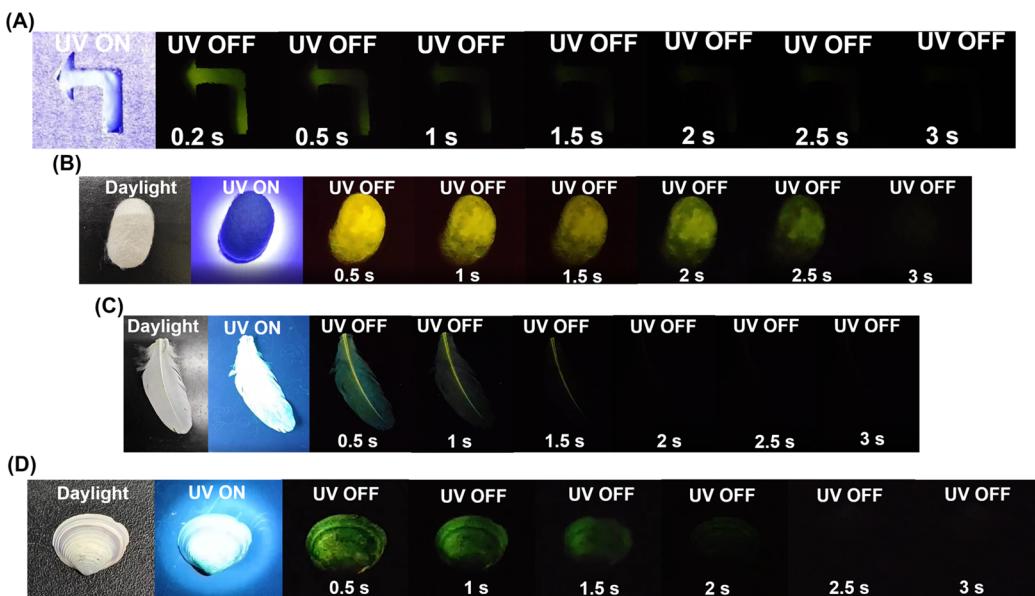


Figure 5. (A) Left turn indicator light made of 2-SCS afterglow materials. (B) Photographs of whole 2-SCS samples at UV-ON and UV-OFF states. (C) Photographs of 2-Feather samples at UV-ON and UV-OFF states. (D) Photographs of 2-Shell samples at UV-ON and UV-OFF states.

ditions, as oxygen in the polymer matrix can quench the triplet excited state of luminescent dopants. After sufficient irradiation, oxygen in the polymer matrix can be removed and activated, exhibiting significant room-temperature phosphorescence. However, natural silkworm cocoon silk shells can effectively immobilize BF_2bdk molecules in a rigid environment within a three-dimensional network (Figure S17). This framework limits the nonradiative decay and oxygen quenching of triplet excitons and promotes ISC, ensuring phosphorescence emission. Second, the main component of SCS is proteins, which contain amide bonds that can form hydrogen bonds, effectively preventing the entry of oxygen. The BF_2bdk -SCS materials have long afterglow properties due to the protection of the matrix. After vacuuming it, water and oxygen are better removed, thus increasing the phosphorescence lifetime (Figure S18).⁷⁰

SCS is a natural biological source, for which preparing afterglow materials only needs a small amount of BF_2bdk . Therefore, the BF_2bdk -SCS material is considered sustainable with great potential for application. In addition, we fed the silkworms with mulberry leaves coated with a suspension of BF_2bdk (Figure 4A). When the silkworms started spinning silk, we observed room-temperature phosphorescence of the silkworm silk. After the UV lamp was turned off, we observed the appearance of organic room-temperature persistent luminescence. Although the luminescence was very weak, future prospects for applications in displays, sensors, and biomedical application are undoubtedly promising. Additionally, we soaked raw silk in BF_2bdk -ACE for 2 h and then evaporated the solvent (Figure 4B). Natural raw silk thread and silk doped with BF_2bdk can produce afterglow characteristics, indicating that protein threads can be used for the biomedical implants field. Under UV lamp excitation, organic persistence luminescence was observed for up to 1 s. Natural silk is widely available and can serve as an excellent matrix. Therefore, the prospect of using natural silkworm cocoon silk to prepare organic room-temperature persistent luminescent

materials is broad, and it is believed that in the near future, it will be truly useful for people.

We used compound 2 as a luminescent dopant and different natural products, such as silkworm shells, as a matrix for functional demonstrations. We unfolded the RTP SCS and presented an exit sign together with a pattern with a left turn indicator (Figure 5A). Also using an entire silkworm shell as the matrix, a yellow-green phosphorescence was emitted under UV lamp excitation with a phosphorescence lifetime of 251.7 ms (Figure S19), demonstrating the integrity of the obtained luminescent material (Figure 5B). After washing with water, it can still maintain its afterglow characteristics (Figure S20). Additionally, using natural pigeon feathers and shells as matrices, the excitation decay curve of 2-Feather monitored at 525 nm showed an emission lifetime of 246.7 ms (Figure S21), while 2-Shell had a phosphorescence lifetime of 316.9 ms (Figure S22), with both organic persistence luminescence lasting for 2 s (Figure 5C,D). Compound 2, as a luminescent molecule, can be doped into matrix materials based on these three proteins to produce afterglow properties. However, due to the high protein content of SCS, 2-SCS has strong afterglow characteristics. The protein in feathers is relatively loose, and the protein content in shells is low, so the afterglow performance of both is weaker than that of 2-SCS. Overall, it is evident that natural products as luminescent matrices have promising future applications in the biological field.

In conclusion, we report a method for preparing organic afterglow silk using natural product silkworm cocoon silk and a doping matrix design strategy. A two-component natural product RTP material was fabricated by directly processing and feeding silkworms with leaves containing the functional materials BF_2bdk , also using raw silk, natural feathers, and shells as matrices. The natural silkworm cocoon silk shell matrix provides a rigid environment for the BF_2bdk triplet to suppress its nonradiative decay and oxygen quenching. Therefore, the successful preparation of natural silk by room-temperature phosphorescence is an innovative multifunctional silk material that meets the requirements of new biomedical

applications. This more environmentally friendly strategy can easily expand the scale, paving a new path for the large-scale production of sustainable advanced silk materials. Additionally, since BF_2bdk -SCS with extended applicability can potentially be produced on a large scale using this effective and greener strategy, further studies should be carried out in the future to understand how the feeding materials influence the silkworm larvae growth and how organic afterglow and phosphorescence lifetime can be extended.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.4c00526>.

Materials; synthesis of compounds 0, 1, and 2; RTP material preparation; the process of feeding silkworms; structural characterization results, including ^1H NMR, ^{13}C NMR, ^{11}B NMR, ^{19}F NMR, LRMS, HRMS, FTIR (Figures S23–S43), HPLC (Figure S16), SEM (Figure S17), UV-vis (Figure S1), single crystal structure (Figure S44), isosurface maps of electron–hole density difference (Figures S11–S13), excitation spectra (Figures S10, S14), photographs under UV lamp and spectra (Figures S2–S9, S15, S18–S22), etc.; and computational methods ([PDF](#))

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Author Contributions

#X.P. and X.L. contributed equally to this work. CRediT: Xixi Piao data curation, methodology, writing—original draft; Xun Li data curation, visualization; Guangming Wang visualization; Tengyue Wang visualization; Kaka Zhang conceptualization, funding acquisition, supervision, writing—review and editing.

Notes

The authors declare no competing financial interest.

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