Purely Organic Blue Room-Temperature Phosphorescence Activated by Acrylamide In Situ Photopolymerization

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Purely organic room-temperature phosphorescence (RTP), especially blue phosphorescence, has aroused considerable attention in organic optoelectronic applications. Herein, a purely solid supramolecular assembly with blue phosphorescence is constructed by 6-bromoisoquinoline-modified β -cyclodextrin (CD-IQ), acrylamide (AAm), and cucurbit[7]uril (CB[7]) based on in situ photopolymerization strategy, accompanied by blue RTP emission at 450 nm. The abundant hydrogen-bonding network between the formed polyacrylamide matrix and the β -CD effectively restricts the motion of the 6-bromoisoquinoline chromophore and suppresses the nonradiative transition, realizing purely blue RTP emission. As compared with CD-IQpolymer, supramolecular assembly between CB[7] and CD-IQ can improve the quantum yield and lifetime from the initial 25.5% and 238.47 ms to 49.41% and 268.9 ms, respectively, which is attributed to the confinement effect of the cucurbituril hydrophobic cavity, and can be further applied in fields of anti-counterfeiting, information encryption, and writing.

1. Introduction

Recently, highly efficient and stable room-temperature phosphorescence (RTP) materials with long-lived excited states in purely organic systems have aroused considerable attention for their important applications in display technology,^[1] optoelectronics,^[2] lighting,^[3] and sensors.^[4] Different from fluorescent materials, the phosphorescence-based organic materials possess a long emission lifetime and afterglow, large Stokes shifts, and rich triplet states, thus exhibiting unique optoelectronic properties.^[5] However, achieving effective RTP emission under ambient conditions is not an easy task, since triplet excitons could be easily deactivated through the vibration and rotation of organic chromophores or invasion of moisture and oxygen.^[6] Therefore, enhancing the intersystem crossing rate to populate triplet excitons and simultaneously effectively suppress the nonradiative decay processes is crucial to achieve the long-lived

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excited states for RTP materials.^[7] Based on the aforementioned principles, many intriguing long-lived RTP systems have been developed, including the introduction of heavy atoms or other heteroatoms into an organic molecule to boost triplet excitons by enhancing spin-orbital coupling.^[8] In the meantime, crystallization,^[9] metal-organic frameworks,^[10] embedding of organic phosphors into a rigid polymer matrix,^[11] host-guest interactions,^[12] hydrogen bonding,^[13] formation of H-aggregation and polymerization have been used to minimize nonradiative relaxation and effectively enhance RTP.^[14] Although breakthrough results have been achieved by various enhancement strategies, RTP materials, especially suitable materials for making purely blue phosphorescence remain guite scarce. Recently, a new confining isolated chromophores

strategy has been developed to achieve high-performance blue phosphorescence. Huang and co-workers demonstrated that the confinement of an isolated chromophore in ionic crystals enabled the tunable phosphorescence from blue to deep blue by changing the charged chromophores and their counterions.^[15] Subsequently, they proposed a feasible ligand functionalization strategy using metal-organic frameworks as a model to develop blue phosphorescent materials with high efficiency and long lifetime simultaneously under ambient conditions.^[16] Although non-radiative transition induced by molecular motion can be suppressed by crystal states to promote phosphorescence, the cultivation of crystal-based chromophores has poor reproducibility and a harsh growth environment, which makes the development of long-lived blue luminophores challenging and greatly hinders their development in practical applications.

Notably, acrylamide (AAm) as a rigid amorphous matrix can well inhibit the molecular motions, of which copolymer materials have good stability based on abundant hydrogenbonding interactions and will offer strict rigid environments for organic phosphors. For example, Tian and co-workers reported a class of copolymers prepared from AAm, whose cross-linked hydrogen-bonding network anchors the phosphors, provides a microenvironment for shielding quenchers, and effectively improves the phosphorescence lifetime and quantum yield.^[17] More recently, we obtained a series of long-lived room temperature phosphorescent materials based on AAm copolymers.^[18] On the other hand, many host-guest strategies have



Scheme 1. Schematic illustration for the highly efficient blue RTP from hydrogen-bonding network of CD-IQ-polymer and CD-IQ/CB[7]-polymer.

been used for phosphorescent materials, which provide crucial roles in enhancing phosphorescence lifetime and quantum yield. Among them, cucurbit[n]urils (CB[n], n = 5–8, 10, 14) are a class of macrocyclic host molecules with a hydrophobic cavity that can assemble with many guest molecules driven by the ion-dipole interaction.^[19] To date, CB[n] and its derivatives have been widely used to construct phosphorescent systems. Nonetheless, to our knowledge, efficient blue phosphorescence emission via copolymers or host-guest strategy is relatively rare, as this may dissipate triplet excitons through triplet-triplet annihilation and lead to a red-shift of phosphorescence.

Here, we developed a concise approach to prepare highly efficient RTP materials via facile in situ photopolymerization by doping 6-bromoisoquinoline-modified β -CD (**CD-IQ**) into AAm, in which 6-bromoisoquinoline was selected as the chromophore center (**Scheme 1**). To our surprise, the abundant hydrogen-bonding network between the formed polyacrylamide matrix and the β -CD effectively restricted the motion of the 6-bromoisoquinoline chromophore and suppressed the non-radiative transition, resulting in a significant blue shift of the chromophore. At the same time, heavy atoms facilitate the ISC from singlet-excited states to triplet-excited states and increase

triplet excitons, thereby realizing purely blue RTP emission with a phosphorescence quantum yield of 25.5% and lifetime of 238.47 ms under ambient conditions. The blue afterglow can last \approx 2 s after removing excitation (video S1, Supporting Information). In addition, after complexing with CB[7] via host-guest interaction, the quantum yield and lifetime are improved to 49.41% and 268.9 ms, respectively, which can be attributed to the confinement effect of the hydrophobic cavity.

2. Results and Discussion

First, **CD-IQ** was synthesized by nucleophilic substitution and fully characterized by nuclear magnetic resonance (NMR), high-resolution mass spectrometry, and high-performance liquid chromatography (Scheme S1, Figures S1–S8, Supporting Information).^[20] Thereafter, it was introduced into an amorphous acrylamide matrix to achieve long-lived blue phosphorescent material after photo-initiated polymerization in situ for 1.5 h and drying for 3 h. During the polymerization process, a large amount of acrylamide monomers were polymerized to form a three-dimensional network structure, and the inter/intramolecular





Figure 1. a) SEM image of dried **CD-IQ**-polymer. b) FT-IR spectra of **CD-IQ**-polymer at different doping concentration (0.3–1 mg ml⁻¹). c) The CIE coordinate of **CD-IQ**-polymer according to the CIE 1931 chromaticity. d) The photographs of **CD-IQ**-polymer excited with a UV lamp (254 nm) and then turned off.

hydrogen bonding network between acrylamide chains and the chromophores effectively confined the molecular motion, protecting these chromophores from oxygen and water quenching, thereby suppressing the nonradiative decay of excited triplet excitons. The amorphous morphology of CD-IQ-polymer was characterized by powder X-ray diffraction (Figure S9, Supporting Information). Figure 1a presents the SEM images of CD-IQ-polymer prepared by polymerization, showing the clear three-dimensional porous network structure. Subsequently, the formation of CD-IQ-polymer was further confirmed by Fourier transform infrared (FT-IR) spectroscopy (Figure 1b). The FT-IR spectra presents the characteristic absorption of amides at 3325.64 cm⁻¹, 3183.52 cm⁻¹, 1646.36 cm⁻¹, and 1604.85 cm⁻¹. Moreover, the peak at 3307 cm⁻¹ was assigned to the stretching vibration peak of -OH, and the peaks in the 1200-1000 cm⁻¹ region were the characteristic peaks of the glucose ring, which proved that CD-IQ was contained in the materials.

The photophysical properties of **CD-IQ**-polymer with different doping concentrations (i.e., 0.3, 0.5, and 1 mg mL⁻¹) were investigated in detail by prompt and delayed spectra and time-resolved decay plots. Both the steady-state (prompt) photoluminescence spectrum and the time-resolved (delayed) spectrum of **CD-IQ**-polymer showed the blue emission around 450 nm (emission wavelengths of 0.3–1 mg mL⁻¹ doping concentration are 451 nm, 448 nm, and 450 nm, respectively) (**Figure 2**a,b, and Figures S10–S13, Supporting Information). Under ambient conditions, the phosphorescence lifetimes of **CD-IQ**-polymer with doping concentrations of 0.3-1 mg mL⁻¹ around 450 nm were 238.47 ms, 249.69 ms, and 256.55 ms, respectively (Figure 2c, Figures S14 and S15, Supporting Information).

The phosphorescence quantum efficiency of **CD-IQ**-polymer reached 25.5%, 23.2%, and 19.3%, respectively (Figure 2d, Figures S16 and S17, Supporting Information). Both PL and phosphorescence spectra showed dominant emission bands at approximately 450 nm under excitation from 260 to 300 nm (Figure 2e), indicating that the phosphorescence emission is very stable under the excitation of various wavelengths in the UV region. In addition, the phosphorescence properties of **IQ** (diluted solution at 77 K) and **CD**-AAm polymer (without **IQ**) were performed (Figures S18–S21, Supporting Information). Further, confirm the blue phosphorescence emission at 450 nm mainly originates from the confinement of the 6-bromoisoquinoline chromophore in the hydrophobic environment of the complex polymer hydrogen-bonding network.

The temperature sensitivity was also investigated by varying the temperature from 107 K to 297 K and measuring the steadystate and delayed (at fixed delay of 100 µs) emission spectra (delay spectra only shows data for 127-297 K). Phosphorescence intensity and lifetime showed a decreasing trend with increasing temperature, ruling out the possibility of assigning the emission band at 451 nm to thermally activated delayed fluorescence, suggesting that phosphorescence is the dominant radiation decay channel at room temperature (Figure 3a-c). Impressively, the blue afterglow exhibited by CD-IQ-polymer was recognizable by the naked eye even in sunlight (video S2, Supporting Information). In a control experiment by introducing 6-bromoisoquinoline into the polyacrylamide matrix (IQ-polymer), the steady-state spectrum showed a yellow emission at 542 nm, which was quite different from the blue phosphorescence of CD-IQ-polymer (Figure S22, Supporting







Figure 2. a) Absorption and photoluminescence spectra of **CD-IQ**-polymer at 0.3 mg ml⁻¹ doping concentrations. b) Prompt and delayed phosphorescence spectra of **CD-IQ**-polymer at 0.3 mg ml⁻¹ doping concentrations. Excitation by 301 nm, delayed time: 10 ms. c) Lifetime decay curve for the phosphorescence emission peak of **CD-IQ**-polymer at 451 nm. d) Phosphorescence quantum yield of **CD-IQ**-polymer (integrated region: 376–642 nm). e) Excitation-phosphorescence emission mapping of **CD-IQ**-polymer under ambient conditions.

Information). In addition, the phosphorescence quantum yield of IQ-polymer was measured to be 22.63% (Figure S23, Supporting Information). Considering the polyhydroxy rigid structure of the cyclodextrin moiety, we deduce that the three-dimensional hydrogen bond network between acrylamide and cyclodextrin inhibited the molecular motion and prevented the stacking among molecules. Notably, the phosphorescent emission could be blue-shifted in the single-molecule state, but not in its aggregated state. A possible reason may be that the confinement of isolated chromophores in a rigid matrix with minimal nonradiative transitions might significantly improve the blue phosphorescence efficiency.

As reported in previous literature, CB[*n*]s could complex with some positively charged phosphorescent guest molecules and

enhance their phosphorescence intensity in the solid state.^[21] First, the host-guest binding mode of CB[7] and **CD-IQ** was investigated by Job's plot, and the result showed a 1:1 binding stoichiometry. The binding constant was determined to be 1.84×10^5 M⁻¹ by UV titration (Figures S24 and S25, Supporting Information). Moreover, the ¹H NMR experiment also provided evidence for the inclusion complexation. With the gradual addition of CB[7] into the aqueous solution of **CD-IQ**, peaks related to protons Ha, Hb, Hc, Hd, and Hf of **CD-IQ** all underwent upfield shifts. When the amount of CB[7] was increased to >1 eq., the proton chemical shift no longer changed. The final chemical shifts for Ha, Hb, Hc, Hd, and Hf were 1.577 ppm, 0.525 ppm, 1.68 ppm, 0.366 ppm, and 0.288 ppm, respectively (**Figure 4**). These results suggested that the **IQ** unit was





Figure 3. a,b) Steady-state photoluminescence spectra from 107 to 297 K and delayed (delay = $100 \ \mu$ s) photoluminescence spectra from 127 to 297 K. c) Temperature-dependent transient photoluminescence decay of the **CD-IQ-**polymer.

included in the hydrophobic cavity of CB[7] to form the stable host-guest complex. After complexing CB[7] with **CD-IQ** at the same concentration in aqueous solution, the corresponding supramolecular polymer (**CD-IQ**/CB[7]-polymer) was obtained by the same preparation method (the doping concentrations were 0.3 mg mL⁻¹, 0.5 mg mL⁻¹, 1 mg mL⁻¹, respectively).

The photophysical property of **CD-IQ**/CB[7]-polymer under ambient conditions was also investigated and compared with that of **CD-IQ**-polymer. The phosphorescence peaks of



Figure 4. ¹H NMR titration spectra of **CD-IQ** in the presence of (a) 0.00, (b) 0.40, (c) 0.60, (d) 1.00 equiv. of CB[7] (400 MHz, D_2O , 298K, [**CD-IQ**] = 1.0 mM).

CD-IQ/CB[7]-polymer were basically consistent with that of CD-IQ-polymer and still maintained the good blue phosphorescence emission, proving that CB[7] had no effect on the energy level of chromophore (Figure 5a). The prompt and delayed spectra of CD-IQ/CB[7]-polymer were well overlapped, indicating a higher phosphorescence efficiency (Figure 5b). Besides, the time-resolved decay spectra and quantum yield results demonstrated that the phosphorescence quantum yield of CD-IQ/CB[7]-polymer was 49.41% with a lifetime of 268.9 ms (Figure 5c,d). This phosphorescence quantum yield was quite higher than that of CD-IQ-polymer (25.5%) (Figures S26 and S27, Supporting Information). To further determine the phosphorescence property, we performed a temperature-sensitive phosphorescence test. As the temperature increased from 77 K to 297 K, the steady-state and delayed spectra (at fixed delay of 100 µs) intensity decreased to some extent, and the phosphorescence lifetime also decreased from 348.8 ms at 127 K to 268.6 ms at 297 K, which confirmed the supramolecular polymer emitted phosphorescence rather than thermally activated delayed fluorescence (Figures S28-S30, Supporting Information). Nanosupramolecular assembly of CD-IQ with CB[7] enhanced the phosphorescence emission intensity of supramolecular polymers by a factor of nearly 4 at room temperature (Figure 5e). In addition to the rigid environment provided by the polymer, the strict encapsulation of CB[7] also played a crucial role, which together prevented the nonradiative relaxation and facilitated the intersystem crossing. Moreover, there was still blue afterglow lasting for above 2s after withdrawing UV light (video S3, Supporting Information), effectively verifying the good efficiency of CB[7] for improving the phosphorescence







Figure 5. a) Absorption and photoluminescence spectra of CD-IQ/CB[7]-polymer at 297 K. b) Prompt and delayed phosphorescence spectra of CD-IQ/CB[7]-polymer. Excitation by 306 nm, delayed time: 10 ms. c) Lifetime decay curve for the phosphorescence emission peak of CD-IQ/CB[7]-polymer at 450 nm. d) Phosphorescence quantum yield of CD-IQ-polymer (integrated region: 378–644 nm). e) Photoluminescence spectra before and after adding CB[7] to CD-IQ-polymer.

efficiency and lifetime. Similar results were obtained for polymers with other doping concentrations (Figures S31–S36, Supporting Information). In addition, the photophysical properties of CD-IQ and CD-IQ/CB[7] also were measured. As shown in Figures S37–S40, Supporting Information, compared with **CD-IQ**, the introduction of cucurbituril enhanced the emission intensity at 537 nm by nearly 10 times, the corresponding quantum yield increased from the initial 3.92% to 6.48%, and the lifetime also increased from the initial 2.92 μ s raise to 2.28 ms.

To demonstrate the generality of our efficient blue phosphorescence approach, we synthesized another cyclodextrin derivative, 4-(4-bromophenyl)-pyridine-modified β -CD (**CD-PY**) (Figures S41–S43, Supporting Information). The introduction of **CD-PY** phosphor into acrylamide matrix also exhibited the blue phosphorescence similar to that of **CD-IQ** phosphorescent material after photopolymerization. The steady-state PL and phosphorescence spectra of the **CD-PY**-polymer showed an emission peak at 472 nm (Figures S44 and S45, Supporting Information). In addition, we found that the **CD-PY**-polymer also had a relatively long phosphorescence lifetime and quantum yield. The time-resolved decay spectra and quantum yield results demonstrated that the phosphorescence quantum yield was 25.38% and the lifetime was 212.97 ms (Figures S46 and S47, Supporting Information). After associating **CD-PY** with cucurbituril,^[22] the **CD-PY**/CB[7]-polymer exhibited similar properties to **CD-IQ**/CB[7]-polymer, that is, the addition of CB[7] did not significantly affect the emission peak shift and phosphorescence quantum yield (Figures S48–S51, Supporting Information).





Figure 6. a) Schematic illustration of the application for information encryption. b) Morse code comparison table. c) "N" and "K" written on a glass plate stand for "Nan Kai".

Next, we demonstrated the potential of these phosphors in information encryption by incorporating Morse code (Figure 6a), where the words "I love you" and "I hate you" were encrypted through Morse code. In daylight, only colorless patterns were obtained. When the UV lamp exciting at 254 nm was turned on, the intense yellow fluorescence and the blue phosphorescence appeared. If the yellow fluorescence was used as the standard, the meaning of the sentence was "I hate you", but if the blue phosphorescence was used as the standard, the meaning of the sentence was "I love you". At this time, it is impossible to distinguish the true meaning of the sentence. When the UV light was turned off, the yellow fluorescence disappeared immediately due to its short lifetime, while the Morse code-encrypted "I love you" words appeared in the form of long-lived blue phosphorescence. Therefore, we realized the encoding of information encryption and anti-counterfeiting by cleverly utilizing the long lifetime of blue phosphors combined with Morse code. In addition, supramolecular polymers could be applied in writing (Figure 6c).^[23] The pre-prepared assembly solution was written on a glass plate after photopolymerization. After drying, it showed the blue light emission under 254 nm light. After turning off the excitation source, the naked eye could capture the blue afterglow effect of ≈ 2 s.

3. Conclusion

In summary, a facile long-lived RTP system was developed through an in-situ photopolymerization strategy based on acrylamide with **CD-IQ** and macrocyclic compound CB[7]. Impressively, the assembly showed efficient blue phosphorescence emission at 450 nm with a lifetime of up to 268.9 ms and a quantum yield of up to 49.41% under ambient conditions.

Experiments show that the rigid environment established by the rich hydrogen-bonding network and the host-guest effect between chromophore and cucurbituril can effectively suppress the nonradiative decay and prevent the quenching of triplet excitons, thereby confining the isolated chromophores to achieve the efficient blue phosphorescence. It is worth mentioning that we have successfully applied this ultra-long blue phosphorescent material to digital encryption, writing, and other fields. This study provides an efficient route to develop various blue RTP materials, paving the way for high-performance organic phosphors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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