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Non-Covalent Iron-Armored Chain Horse: A Strategy Leading to Highly Efficient Deep-Blue Room Temperature Phosphorescence

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The iron-armored chain horse is a military strategy in ancient China to enhance the combat force of the entire army, especially when individual fighters are vulnerable to being picked off one by one. Herein, this strategy is adopted to generate highly efficient metal-free blue room temperature phosphorescence (RTP) using the world's largest production of dicarboxylate acid. By encapsulating the commercially available chemical disodium terephthalate (DTPA) within the iron armor of α -cyclodextrin (α -CD), and subsequently linking the iron-armored DTPA@ α -CD horses into a crystalline array mediated by hydrogen bonds and Na⁺ coordination, a highly confined and segregated arrangement of DTPA is achieved, leading to heavy atom-free deep-blue phosphorescence with a maximum efficiency of 83.3%. Since the crystalline array of the iron-armored chain horse DTPA@ α -CD can be facilely obtained through water evaporation, the current phosphorescent material allows for rapid, high-throughput solution processing of deep-blue afterglow display, offering an economic and environmentally benign approach for deep-blue RTP materials and facilitating their application.

1. Introduction

Organic room temperature phosphorescence (RTP) materials have garnered significant interest in recent decades owing to their easy modification, processability, and biocompatibility. These properties make them suitable for various applications, including organic luminescence emission diode(OLED),^[1] sensors,^[2] data encryption,^[3] and bioimaging.^[4]

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DOI: 10.1002/adom.202400920

In the last decade, numerous colorful organic RTP materials have been developed through diversified methods such as crystallization.^[5] H-aggregation.^[5c,f,6] host-guest doping,^[7] polymerization,^[8] and others.^[2a,3a,9] In most cases, these strategies would lead to green and yellow phosphorescence with an emission wavelength in the range of 450-600 nm. due to the unavoidable intermolecular coupling between chromophores.^[5c,f,6b] In contrast, blue RTP materials with an emission wavelength ranging from 400 to 450 nm are still scarce because it is difficult to retain a high triplet energy level and suppress rampant non-irradiative decay under ambient conditions.^[10]

To date, tremendous efforts have been made to obtain blue RTP materials.^[8e,9c,11] Among these endeavors, immobilizing chromophores in a single molecular state has been proven to be effective.^[11a,b,d,e] An example of this

is the construction of pillar-layer MOFs by Wang et al., which involves isolating chromophores with the help of predefined coligands and restricting molecular motions by introducing guests with steric effects.^[11b] Alternatively, Huang et al. achieved highperformance blue phosphorescence through the formation of ionic crystals, where highly charged chromophores are isolated from each other and tightly confined through high-density ionic bonds.^[11a] Chemical strategies were also employed to achieve blue RTP.^[11c,12] For instance, Li et al. modified the molecular structure of chromophores to decrease intermolecular interactions in crystals.^[11c] Despite these extraordinary contributions, critical crystal engineering or molecule design is required to achieve the simultaneous confinement and segregation of chromophores. In addition, heavy atoms are typically incorporated into the phosphors to enhance spin-orbital coupling (SOC) and facilitate intersystem crossing.^[8e] So far, it still remains challenging to create heavy atom-free and efficient blue RTP materials through simple and environmentally benign non-covalent approaches.

Herein, we present a straightforward non-covalent ironarmored chain horse strategy to achieve efficient blue RTP from disodium terephthalate (DTPA), the world's largest production of dicarboxylic acid. The "horse" DTPA was iron-armored with α -cyclodextrin, an economic macrocycle available at industrial



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Non-Covalent Iron-Armored Chain Horse



With armor and chains on, we are shining blue RTP!

Scheme 1. Schematic illustration of the non-covalent iron-armored chain horse strategy for efficient deep-blue RTP. Inspired by the military strategy of the iron-armored chain horse in ancient China, the chromophores are first armed with cyclodextrins and then chained into rigid lattice through non-covalent interactions. This strategy leads to chromophores' isolation and immobilization simultaneously, which strictly avoids intermolecular coupling and restricts non-radiative transition, contributing to highly efficient deep-blue RTP.

scale, through host-guest interaction. The crystalline assembly of the "iron-armored horses" DTPA@ α -CD, driven by hydrogen bonds and coordination of Na⁺ with the hydroxyl group, allows them to be "chained" into an entire array, leading to effective isolation and immobilization of DTPA. Since the carbonyl groups of DTPA facilitate SOC, the heavy atom-free iron-armored chain horse of DTPA emits deep-blue RTP with a lifetime of 215 ms and an extremely high quantum yield of 83.3%. Moreover, the current deep-blue RTP materials can be used as water-based ink for high-throughput afterglow displays. This not only significantly reduces the barrier to creating deep-blue phosphorescent displays, but also provides a simple approach for their production and application on an industrial scale. (Scheme 1)

2. Results and Discussion

DTPA (Figure 1a) is a conventional phosphor owned by the SOC promoted by carboxyl groups. However, DTPA powders only emit an UV fluorescence centered at 355 nm, accompanied by a very weak green phosphorescence of aggregates (QY_{phos} $\approx 0.17\%$) due to the rampant non-radiative transition under ambient conditions and self-quenching effect (Figure 1b; Figures S1 and S2, Supporting Information). It is noticed that the phosphorescence spectra of a dilute DTPA solution in a frozen state largely blueshift by \approx 90 nm compared to that of DTPA powders, exhibiting a deep-blue phosphorescence of monomers centered at 420 nm (Figure 1b; Figure S3, Supporting Information). Since DTPA is the sodium salt of the world's largest dicarboxylate, if this phosphorescence of monomers can be obtained at room temperature, it will allow the creation of deep-blue RTP materials in a facile and scalable way.

In order to obtain the deep-blue RTP of DTPA, restricting its thermal motion is crucial. To this goal, α -CD was added to

the aqueous solution of DTPA. Because the width of the DTPA molecule matches well with the diameter of the cavity of α -CD (Figure 1a), "armoring" DTPA by encapsulating it into the cavity of α -CD is expected. 2D NMR (ROESY) spectrum reveals a correlation between the benzene protons of DTPA and the inner wall protons of α -CD (H3, H5), indicating that the benzene ring of DTPA is indeed "armored" in the cavity of α -CD (Figure 1c). High-resolution mass spectrometry reveals the presence of the complex with host: guest molar ratio of 1:1 (Figure S4, Supporting Information). However, low temperature is still required to obtain blue phosphorescence (Figure 1d). This is because the host-guest complex of α -CD and small guest molecules is usually dynamic so the in-and-out exchange of the guest keeps going on in solution.^[13] It is worth noting that in the frozen state, the phosphorescence spectra exhibit fine structures even in the concentrated DTPA@ α -CD solution of 1×10^{-1} M, manifesting that the "iron armor" α-CD has simultaneously restricted and isolated the DTPA molecules. This inspires that if the "iron-armored" DTPA@a-CD complexes are further chained into crystalline arrays where the exchange of DTPA molecules is strictly forbidden, the desired deep-blue phosphorescence can be obtained at room temperature.

Next, further "chaining" the "iron-armored" DTPA@α-CD complexes into crystalline arrays was achieved by slowly evaporating the aqueous solution of DTPA@α-CD at room temperature (25 °C). Figure 2a shows the photo of the obtained crystalline grains, which were expected to be driven by the hydrogen bonding between cyclodextrins.^[5e,14] These crystalline grains are drastically different in shape from the rectangular α -CD crystals obtained by evaporating α -CD aqueous solution (Figure S5, Supporting Information). FT-IR measurements reveal that the characteristic asymmetric (v_{as}) and symmetric stretching vibrations ($v_{\rm s}$) of COO[–] and bending vibration of Ar-H ($\delta_{\rm Ar-H}$) of DTPA were significantly reduced and even completely vanished in the acquired crystalline material, indicating that the vibrations of these bands were restricted (Figure 2b). This result is consistent with the fact that DTPA was threaded into the cavity of α -CD.^[15] Powder X-ray diffraction (XRD) measurements (Figure 2c) reveal that the crystalline DTPA@α-CD material exhibited strong diffraction peaks distinct from DTPA powder and the pristine cage-type α -CD crystals.^[16] The presence of a prominent diffraction peak at 20.0° further indicates the formation of a channel-type array of α -CD in the crystalline material.^[16,17] Figure 2d shows the steadystate fluorescence and phosphorescence spectra of the crystalline material. They are nearly overlapping with each other and both exhibit a structured blue emission at 405 nm. This emission is identical to that for the cryogenic DTPA@α-CD solution, indicating that the non-radiative decay of DTPA has been significantly inhibited in the crystalline material under ambient conditions.

The phosphorescent nature of DTPA in the crystalline material was further confirmed through temperature-dependent PL measurement. As the temperature increased from 100 to 300 K, the emission intensity and lifetime kept decreasing (Figure S6, Supporting Information), which excluded the possibility of thermal-activated delayed fluorescence (TADF).^[18] The excitation-phosphorescence emission mapping demonstrates that the material can be efficiently excited by UV light ranging from 265 to 295 nm (Figure 2e), and the color coordinates of the phosphorescence are (0.156, 0.066), which are located in the SCIENCE NEWS _____



Figure 1. Photophysical characterizations of DTPA and DTPA@ α -CD complex. a) Molecular structures and sizes of DTPA and α -CD. b) prompt and delayed (a delayed time of 0.1 ms) photoluminescence (PL) spectra of DTPA powder (up, $\lambda_{ex} = 310$ nm) and 1×10^{-5} M DTPA aqueous solution (down, $\lambda_{ex} = 280$ nm, 77 K). c) 2D NMR (ROESY) of DTPA@ α -CD solution (600 MHz, D₂O), the above is the schematic illustration of host-guest complexation between DTPA and α -CD. d) prompt and delayed (a delayed time of 0.1 ms) PL spectra of 0.1 M DTPA@ α -CD aqueous solution ($\lambda_{ex} = 280$ nm, 77 K). The insets in (b) and (d) are photos taken under 280 nm UV light.

deep-blue region and quite close to pure blue light (0.140, 0.080) (Figure 2f).

The molar ratio of host to guest would influence the crystalline structure in the solid state and the corresponding phosphorescent performance. By maintaining a constant concentration of DTPA (50 mm) and adjusting the amount of α -CD added to the solution, crystalline materials were obtained for all of these systems through the gradual evaporation of water. Figure 3a reveals that both phosphorescence quantum yield (QY_{phos}) and phosphorescence lifetime ($\tau_{\rm phos}$) display a maximum value when the feeding ratio of α -CD to DTPA varies between 0.25 and 4. The nonradiative decay rate constant (K_{nr}) of each sample, which was calculated based on the equation, $K_{nr} = \frac{1-\varphi_{phos}}{\tau_{phos}}$, is shown in the Figure 3b. With a molar ratio of 2:1 of α -CD to DTPA, the system exhibits the lowest value of K_{nr} (0.78 s⁻¹), along with the highest QY_{\rm phos} of 83.3% and a $\tau_{\rm phos}$ of 215 ms. The optimal ratio between α -CD and DTPA appears to deviate from the 1:1 host-guest complexation in solution, suggesting that the crystalline structure may not be solely formed by the iron-armored DTPA@α-CD horses. XRD measurements indicate that the molar ratio of 2:1 α -CD: DTPA was most favorable for generating the channel-type lattice (Figure S7, Supporting Information). However, the lack of α -CD could result in inadequate inclusion of DTPA and potentially cause DTPA to crystallize, while excessive α -CD would lead to the formation of a cage-type lattice of α -CD, which hinders the stacking of DTPA@ α -CD complexes into a channel-type lattice.

In order to directly probe the structure of the crystalline material that displays the optimum deep-blue RTP, a single crystal was grown by slowly evaporating the 2:1 α -CD: DTPA solution over a period of 7 days. The detailed crystal information is presented in Table S1 (Supporting Information). The molar ratio of α -CD to DTPA in the lattice was found to be 2:1, which is consistent with the feeding ratio that corresponds to the optimal phosphorescence performance. As shown in Figure 3c, α -CDs stack into a channel structure in a head-to-tail arrangement driven by intermolecular and intramolecular hydrogen bonding, which is consistent with the results of powder XRD measurements. These channels are held together into crystalline arrays by Na⁺ ions and water molecules, which are situated in the interstices between the channels through coordination interactions and hydrogen bonding. Within the channels, two water molecules and one DTPA molecule are the guests, alternately situated in the neighboring cavities within the channel. DTPA is partially embedded in one α -CD cavity, with one carboxyl group protruding from the wider rim of α -CD and forming hydrogen bonds with the hydroxyl groups in the narrower rim of the adjacent α -CD. Notably, based on the results of single crystal diffraction, DTPA molecules situated in

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Figure 2. Structural and photophysical characterizations of crystalline materials under ambient conditions. a) Optical microscopy image of crystalline grains after water evaporation of DTPA@ α -CD solution. b) FT-IR spectra of DTPA, α -CD, physical mixture of the two and crystalline DTPA@ α -CD materials. c) XRD results of DTPA, α -CD and crystalline DTPA@ α -CD materials. d) Prompt and delayed PL spectra of crystalline DTPA@ α -CD materials (λ ex = 280 nm), insets are photos taken before and after ceasing 280 nm UV light. e) Excitation-phosphorescence mapping (a delayed time of 0.1 ms) of the crystalline DTPA@ α -CD materials. f) CIE 1931 coordinates of crystalline materials' phosphorescence and pure blue light.

the α -CD's channel are twisted with the carboxylate group forming a dihedral angle with the benzene ring, and four possible torsional conformations exist due to the crystal disorders (Figure S8, Supporting Information). Benefiting from the host-guest encapsulation and the crystalline arrays, all the DTPA molecules are "armored" and "chained" together in the rigid matrices. This arrangement not only effectively isolates all the chromophores but also strictly immobilizes them in space.

In order to further explore the origin of the deep-blue phosphorescence, theoretical calculations via first-principle timedependent density functional theory (TD-DFT) were performed on DTPA for both singlet and triplet excited states. The calculated results indicate the spin-orbit coupling matrix elements (SOC) of the torsional conformations are significantly larger than that of the planar conformation, which would facilitate the ISC process to boost phosphorescence generation (Figure 3d; Figure S9, Supporting Information). Based on the above results, we proposed a plausible mechanism for the efficient deep-blue RTP (Figure 3e). Due to the encapsulation by α -CD, the chromophores are well isolated in a monomolecular state in the crystalline assembly. Upon excitation, the generated singlet excitons would facilely transfer to excited triplet states through ISC. With the suppression of the non-radiative transitions through host-guest interaction and crystalline lattice, the triplet excitons would convert to phosphorescence maximally. Therefore, the intrinsic deep-blue phosphorescence of the chromophore is realized under ambient conditions.

The strategy of a non-covalent iron-armored chain horse is crucial for achieving such excellent RTP performance. As we freezedried the same DTPA@ α -CD solution ([DTPA] = 50 mM, [α -CD] = 100 mM), amorphous and fluffy DTPA@ α -CD powder was obtained (Figures S10 and S11, Supporting Information). The resulting phosphorescence band was significantly broadened, indicating that the chromophores were less restricted compared to the crystalline material (Figure S12, Supporting Information). Upon ceasing 280 nm UV light, the afterglow was nearly negligible (Figure 4a). The QY_{phos} and τ_{phos} for the amorphous powder were only 8.44% and 9 ms, respectively (Figure S13, Supporting Information). Consequently, the K_{nr} (101.73 s⁻¹) is 130 times larger than that of the crystalline assembly (0.78 s^{-1}) (Figure 4b). Since the two samples showed very similar water contents according to TGA measurements (Figure S14, Supporting Information), the significantly different phosphorescence performance was not caused by different water contents. Evidently, the crystalline assembly has "chained" the "iron-armored horses" together to significantly restrict the molecular motion of DTPA, which boosts both the efficiency and lifetime of the

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Efficient deep-blue RTP

Figure 3. Mechanistic investigations of the deep-blue RTP. a) The plot of feeding ratios of α -CD to DTPA against QYphos (left) and τ phos (right). b) The plot of molar ratios of α -CD to DTPA against the non-radiative decay rate constant of phosphorescence (Knr). c) Single crystal analysis of the crystalline DTPA@ α -CD materials. d) Calculated energy diagram, SOC values of the low-lying excited states, and NTOs for torsional DTPA. e) Proposed energy transfer processes for the efficient deep-blue phosphorescence.

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Figure 4. Comparison of phosphorescent properties. a) Photos taken before and after ceasing 280 nm UV light for amorphous and crystalline materials. b) Comparison of QYphos, τ phos, and Knr of two materials under ambient conditions. c) Proposed mechanism of iron-armored chain horse strategy for highly efficient deep-blue RTP.

deep-blue RTP. In contrast, for amorphous complex powders, Raman scattering measurements evidence that the chromophores were poorly immobilized due to the absence of a rigid lattice (Figure S15, Supporting Information). Therefore, the triplets' energy is vastly lost through non-radiative transition and the phosphorescence performances are significantly undermined (Figure 4c).

The robust and highly efficient blue RTP enables a wide range of promising applications. Blue RTP luminescent devices can be obtained by simply embedding the material in resin. **Figure 5a** shows the "PKU" patterned deep-blue afterglow emitters by blending the crystalline powder with bisphenol A diglycidyl ether (monomer) and 1,3-diaminopropane (curing agent), indicating its potential application in the deep-blue display industry. Furthermore, the combination of crystalline materials and amorphous freeze-dried powder enables information storage. Under 280 nm UV light, Figure 5b displays the letter "M". However, the pattern changes into the letter "V" after the UV light is switched off, due to the absence of phosphoresce in the amorphous part.

Excitingly, the current DTPA@ α -CD crystalline materials can be applied in the form of an aqueous ink for solution processing. Because the deep-blue RTP can be achieved by naturally evaporating water, the non-phosphorescent aqueous solution containing the DTPA@ α -CD complex can be used directly as ink to write on various substrates. Upon evaporation of water, phosphorescent writings can be created. Figure 5c shows a panda figure drawn with this phosphorescent ink. Under daylight, it was nearly invisible, but it became visible under 280 nm UV light. After the light was turned off, the panda emitted a deep-blue afterglow that lasted for 2 s. The high-quality water-based phosphorescent liquid can also be used to produce phosphorescent paper. Figure 5d shows a rabbit pattern with a deep-blue afterglow by employing the Chinese paper-cutting technique. Inspired by screen printing, we have demonstrated that the ink can be used to create complementary patterns on various substrates, resulting in a pair of complementary artworks with finely matched details. As shown in Figure 5e, when a paper mask with the logo of Peking University was placed on a glass, a pair of complementary phosphorescent logos on both the glass and the paper were created by spraying the ink. Finally, paper treated with phosphorescent ink would yield phosphorescent paper. Because the phosphorescence would vanish immediately when contacting water, dark images can be obtained when writing with pure water. After water evaporation, the phosphorescence recovers, erasing the recorded information. In this way, repeated writing becomes possible. Figure 5f shows that the original "RTP" pattern disappeared after water evaporation and a "heart" pattern was drawn in the same area. The writing/erasing process can be repeated many times since the watergoverned dissolution and crystallization process is completely reversible.

3. Conclusion

In summary, we propose a non-covalent iron-armored chain horse strategy for generating deep-blue RTP, drawing inspiration from a military tactic in ancient China. By using α -CD to arm DTPA molecular horses via host-guest interactions and then chaining the DTPA@ α -CD armored horse in crystalline arrays, we can effectively separate and immobilize DTPA. This process allows us to generate a deep-blue RTP with a high phosphorescence efficiency of 83.3% and a lifetime of 215 ms from the world's most produced dicarboxylic acid. Since the crystalline material can be easily formed through the natural evaporation of water, the non-phosphorescent DTPA@ α -CD aqueous solution can be used as printable phosphorescent ink, demonstrating diversified application possibilities. We envision that the current strategy would open a new paradigm of using simple molecules to create deep-blue RTP materials, making deep-blue RTP display materials easily accessible.



Figure 5. Demonstrations of deep-blue RTP for afterglow display. a) Photos of three letter models "PKU" made by dispersing crystalline powder into epoxyethane and ethylenediamine and then heated at 100 °C b) Photos of a pattern made up of amorphous and crystalline materials showing two different letters before/after turning off 280 nm light. c) Photos of a panda painting with deep-blue afterglow using the DTPA@ α -CD solution as the ink. d) Photos of a rabbit paper cut made from the phosphorescent paper by spraying the solution onto paper. e) Photos of two complementary university logos with deep-blue afterglow made by spraying the solution to a glass substrate covered by a paper mask. f) Transient information recording using water to write in the phosphorescent paper.

Supporting Information

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

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (Grant No. 22172004, 22332001, 21972003) and the Beijing National Laboratory for Molecular Sciences (BNLMS) for financial support.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

crystalline materials, cyclodextrin, deep-blue room temperature phosphorescence, supramolecular assembly Received: April 4, 2024 Revised: May 30, 2024 Published online: July 12, 2024

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