Theoretical investigations reveal the underlying relationship between the proportion of $n$ and $\pi$ orbitals and the rate of intersystem crossing and phosphorescence decay. Accordingly, Tang and colleagues have designed and synthesized a series of full-color pure organic phosphors with an efficiency of up to 36.0% and a long lifetime of 0.23 s under ambient conditions.
Rational Molecular Design for Achieving Persistent and Efficient Pure Organic Room-Temperature Phosphorescence

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SUMMARY
Manipulation of the emission properties of pure organic room-temperature phosphors through molecular design is attractive but challenging. Tremendous efforts have been made to modulate their aggregation behaviors to suppress nonradiative decay in order to achieve efficient light emission and long lifetimes. However, success has been limited. To attain such a goal, here we present a rational design principle based on intrinsic molecular-structure engineering. Comprehensive investigations on the molecular orbitals revealed that an excited state with hybrid (n,π*) and (π,π*) configurations in appreciable proportion is desired. Tailoring the aromatic subunits in arylphenones can effectively tune the energy level and the orbital feature of the triplet exciton. Our experimental data reveal that a series of full-color pure organic phosphors with a balanced lifetime (up to 0.23 s) and efficiency (up to 36.0%) can be realized under ambient conditions, demonstrating the validity of our instructive design principle.

INTRODUCTION
Light is emitted from luminophores and is one of the most fundamental and indispensable elements to life and society. The development of luminophores has greatly promoted high-tech innovations in energy and life sciences. For instance, luminescent materials are widely used in organic light-emitting diodes and biotechnologies. In particular, luminophores with phosphorescent emission can potentially utilize 75% of electrically generated triplet excitons and function as sensitive bioimaging probes to eliminate the short-lived autofluorescence. Indeed, phosphorescent materials have found wide application in electronics, optics, and biological areas. Because the emission from the excited triplet state is sensitive to temperature and oxygen, phosphorescence from a luminophore is normally observed under cryogenic and inert conditions, which has severely restricted its use in high-tech applications. Achieving materials with persistent and efficient room-temperature phosphorescence (RTP) thus has drawn extensive attention. So far, most efficient RTP luminophores are metal-containing inorganic and organometallic compounds, which generally have the drawbacks of high cost and cytotoxicity, low processability, and low flexibility and stability. In contrast, pure organic RTP materials are attractive alternatives and have the advantages of wide variety, good biocompatibility, appreciable stability, and good processability. However, developing persistent and efficient pure organic RTP materials is extremely difficult because of inefficient intersystem crossing (ISC) caused by weak spin-orbit coupling and the rapid rate of nonradiative decay.

The Bigger Picture
The development of luminophores has greatly promoted high-tech innovations in energy and life sciences. For instance, room-temperature phosphorescent (RTP) materials are attractive because of their multidisciplinary applications in electronics, optics, and biological areas. However, developing efficient and persistent RTP materials is extremely challenging for pure organic (metal-free) phosphors because of the weakness of spin-orbit coupling and the sensitivity of triplet excitons. On the one hand, tremendous efforts have been made to modulate aggregation behaviors to suppress nonradiative decay in order to achieve efficient light emission and long lifetimes. On the other hand, the molecular structure and frontier orbital can intrinsically determine their performance but have been poorly investigated. To attain such a goal, here we present a rational molecular design principle based on molecular-structure engineering to serve as a comprehensive model for the exploration of novel organic phosphors.
Recently, several groups have used different methodologies, including polymer aggregation,\textsuperscript{16} crystallization,\textsuperscript{17–21} halogen bonding,\textsuperscript{22,23} self-assembly,\textsuperscript{24,25} and H-aggregation,\textsuperscript{26} to develop pure organic RTP systems (Figure 1). These strategies tend to modulate the aggregation behaviors of organic phosphors to suppress their nonradiative-decay pathways\textsuperscript{27} and thus can be classified as aggregation-induced RTP (Figure 1). Several other important strategies, such as host-guest composition,\textsuperscript{28} polymer-matrix assistance,\textsuperscript{29,30} molecule-metal hybrids,\textsuperscript{31} metal-organic framework hosting,\textsuperscript{32} and so on, are also being investigated and promote the development of the area (Figure 1). Despite these exciting achievements,\textsuperscript{33} there are few examples of organic phosphors with both high efficiency and a long lifetime.\textsuperscript{34–36} It is also quite difficult to explore the strategies further because a comprehensive investigation on the molecular structure-property relationship is lacking.\textsuperscript{37}

Here, we deliver a structure-property relationship from which we derive a molecular design principle on the basis of molecular-orbital investigation. This work provides rational guidelines that will undoubtedly promote the fundamental understanding and exploration of novel pure organic RTP systems from a molecular-structure perspective. Phosphors with high efficiency and long lifetimes, as well as tunable emission, were developed as a proof of concept. The experimental data reveal that balanced RTP performance can be achieved in a single luminogenic molecule.

RESULTS

Molecular-Orbital Model

The Jablonski diagram lists the typical decay pathways of the lowest singlet (S\textsubscript{1}) and triplet (T\textsubscript{1}) excited states (Figure 2A). For obtaining RTP materials with an efficient phosphorescence quantum yield (\(\Phi_p\)) and persistent or long phosphorescence lifetime (\(\tau_p\)), there are three requirements: (1) spin-flipping by an efficient ISC process from S\textsubscript{1} to T\textsubscript{1}, (2) shutdown of nonradiative relaxation or a low rate of nonradiative decay (\(k_{\text{ISC}}\)) to favor phosphorescent emission from T\textsubscript{1} to S\textsubscript{0}, and (3) a slow phosphorescence rate (\(k_p\)) to achieve a long \(\tau_p\) (Equations 1 and 3 in Figure 2).

Phosphors with a high quantum yield of ISC (\(\Phi_{\text{ISC}}\)) generally show a fast ISC rate (\(k_{\text{ISC}}\)) to compete with the rate of fluorescence decay (\(k_f\)) and the rate of internal conversion (\(k_c\)) in the depopulating processes of S\textsubscript{1} (Equation 2 in Figure 2). The \(k_{\text{ISC}}\) can be greatly promoted by small singlet-triplet (S-T) splitting energy and effective spin-orbit coupling (SOC) between S\textsubscript{1} and T\textsubscript{1}. Generally, the S-T splitting energy is large for most organic molecules without a pronounced charge-transfer character. Heavy metals such as Ir and Pt and halogen atoms can trigger significant SOC. On the other hand, for pure organic compounds, according to the El-Sayed rule,\textsuperscript{38} effective SOC occurs in the transition from the singlet state with an electronic configuration such as \(1(p,p\ast)\) or \(3(p,p\ast)\) to a triplet state such as \(3(p,p\ast)\) or \(3(n,n\ast)\), respectively, because the orbitals can effectively overlap under the operation of the orbital angular momentum operator (Figure 2C). In contrast, ISC from \(1(p,p\ast)\) to \(3(p,p\ast)\) and \(1(n,n\ast)\) to \(3(n,n\ast)\) is not favored because the SOC is insignificant as a result of the inefficient orbital overlapping prohibited by the angular momentum operator. Thus, the existence of \(n\) orbitals that are perpendicular to the \(p\) orbitals becomes crucial for triggering striking SOC and turning on the ISC process from the singlet to the triplet state.

Persistent pure organic RTP materials require that \(\tau_p\) shows in a second range and thus need a slow decay process of T\textsubscript{1}. As mentioned, T\textsubscript{1} with a \(3(p,p\ast)\) configuration can show an extremely slow decay rate (\(\sim 10^4 \text{ s}^{-1}\)) because of the forbidden...
transition from $^3(\pi, \pi^\ast)$ to $^1\pi^\ast$. Endowing phosphors with an electronic configuration of $^3(\pi, \pi^\ast)$ is therefore key to obtaining a long-lived $T_1$. However, in pure organic compounds, $T_1$ is rarely either pure $^3(\pi, \pi^\ast)$ or $^3(n, \pi^\ast)$ but is rather a hybrid mixture of the two configurations with different proportions of $\alpha_n^3(n, \pi^\ast) + \beta_p^3(\pi, \pi^\ast)$, where $\alpha_n + \beta_p = 1$ (Figure 2C). The $T_1$ state with a hybrid configuration gives a moderate but tunable $k_P$. Thus, the molecular design of the excited state with hybrid $(n, \pi^\ast)$ and $(\pi, \pi^\ast)$ configurations in appreciable proportion is desired for obtaining efficient persistent RTP materials.

From the above discussion, (1) the existence of $n$ orbitals and (2) the $T_1$ state with a nearly pure $^3(\pi, \pi^\ast)$ configuration are the general structural requirements for developing a pure organic persistent and efficient RTP phosphor without heavy atoms. Following such a molecular design rule, we first chose carbonyl groups (C=O) to provide $n$ orbitals to trigger the ISC from $S_1$ to $T_n$. Then, we incorporated various conjugated subunits to introduce $\pi$ orbitals and reduce $k_P$. Last, five pure organic molecules with molecular structures as shown in Figure 3 were designed and synthesized. Detailed procedures for their synthesis and characterization are given in the Supplemental Information. As expected, the carbonyl groups selected from various heteroatomic groups have $n$ orbitals, which provide effective SOC-induced ISC of $S_1$ to $T_n$, and hence high $\Phi_{ISC}$. Importantly, with the $\pi$-extended subunits, the $T_1$ state has a high character of $^3(\pi, \pi^\ast)$ configuration, resulting in a persistent lifetime. The variation of aryl groups mixes the pure $(n, \pi^\ast)$ and $(\pi, \pi^\ast)$ molecular orbitals, giving tunable $T_1$ states with different energy levels and a $^3(\pi, \pi^\ast)$ character, which in turn affects the phosphorescence color, efficiency, and lifetime. Furthermore, in the crystal state, the vibrational motions are largely suppressed to block the nonradiative decay of $T_1$ as a result of the environmental constraint. Thus, we chose crystallization here as an effective rigidification tool to trigger the RTP by blocking oxygen quenching and other nonradiative-decay pathways. As a result, remarkably
fast $k_{ISC}$, tunable $k_p$, and slow $k_{ISC'}$ can be realized in our system. The $\Phi_p$ of the pure organic molecules prepared can reach 34.5% with a long second-order lifetime.

**Theoretical Calculations**

To validate our assumption and gain more insight into the mechanism of RTP, we performed first-principle density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations on molecules 1–5. For comparison, benzophenone (BP, 6), benzil (7), and difluorobenzophenone (DFBP, 8), whose molecular structures are shown in the Supplemental Information, were also included in the analysis (see section “Theoretical and Computational Methods” in Supplemental Information, Figures S10–S14, and Tables S3–S5). The calculated energy gap ($\Delta E_{S1Tn}$), the SOC constant between $S_1$ and the involved triplet state ($\xi_{S1Tn}$), and the proportions of $^3(n,\pi^*)$ ($\alpha_n$) and $^3(\pi,\pi^*)$ ($\beta_n$) configurations in the $S_1$ and $T_n$ states for 1-(dibenzo[b,d]furan-2-yl)phenylmethanone (BDBF, 3) are given in the inset of Figure 4A; the values for other compounds are provided in Figure S1. From the data, the relationships between $\xi_{S1Tn}$ and $\Delta \alpha_n \left(=\alpha_{n,S1} - \alpha_{n,Tn}\right)$ and $\tau_p$ and $\beta_n$ in the $T_1$ state for 1–8 were established. The calculated energy gaps between $S_1$ and $T_1$ were considerably large for 1–8 (>0.6 eV), which blocks the reversible ISC from $T_1$ to $S_1$ for thermally activated delayed fluorescence and weakens the phosphorescence.40,41

It is easily seen that the extent of SOC, and hence the efficiency of the ISC process from $S_1$ to $T_n$, is really actuated by the characters of the excited states. As shown in
when the \( \Delta \alpha_n \) value became larger, stronger coupling was observed because it promoted \( n \rightarrow \pi \) or single-center \( \rho_n \rightarrow \rho_y \) transition. On the other hand, as described above, the ISC process was also facilitated by a small energy gap (\( \Delta E_{ST} \)) between the two states. This explains why (9H-carbazol-9-yl)(4-chlorophenyl)methadone (ClBCZ, 5) (not given in Figure 4) showed a low \( \Delta \alpha_n \) value but still exhibited quite an efficient ISC process as a result of the narrow energy gap (\( \Delta E_{S1T3} = 0.02 \) eV) between \( S1 \) and \( T3 \). Analysis of the proportions of the \( ^3(n, \pi^*) \) (\( \alpha_n \)) and \( ^3(\pi, \pi^*) \) (\( \beta_n \)) configurations at the \( T1 \) state elucidated the features of the excited states. As depicted in Figure 4B, molecules 6–8 showed a \( \beta_n \) value lower than 50%. Thus, excited states with a predominant \( ^3(n, \pi^*) \) configuration were realized. On the other hand, molecules 1–3 possessed large aromatic subunits. This endowed their excited states with higher \( ^3(\pi, \pi^*) \) characteristics and hence high \( \beta_n \) values above 70%. Generally, molecules with a major \( ^3(n, \pi^*) \) configuration show a faster \( k_P \) and hence a shorter \( t_P \) than those with a \( ^3(\pi, \pi^*) \) configuration because of the availability of the spin-flip process and \( n \rightarrow \pi \) or \( \rho_n \rightarrow \rho_y \) transition. Compound 3 or BDBF, for example, possessed a typical \( ^1(n, \pi^*) \) \( S1 \) state, a low-lying hybrid \( ^3(n, \pi^*) \) and \( ^3(\pi, \pi^*) \) \( T2 \) state, and a typical \( ^3(\pi, \pi^*) \) \( T1 \) state. The relatively smaller energy gap and larger \( \Delta \alpha_n \) value from \( S1 \) to \( T2 \) made the \( S1 / T2 \) transition the key channel to populate the triplet state. The large value of \( \beta_n \) in \( T1 \) suggests its high \( ^3(\pi, \pi^*) \) feature and hence its slow \( k_P \) and long \( t_P \).

**Experimental Investigation**

Benzophenone (6) is an archetypical phosphor and exhibits short-lived (~milliseconds) phosphorescence both in solution at low temperature and in the crystalline state at room temperature. Incorporating different \( \pi \)-extended groups such as benzoyl, benzofuranyl, benzothiophenyl, and carbazolyl groups into its structure afforded five luminophores, namely 1,4-phenylene bis(phenylmethanone) (pDBP, 1), 1,3-phenylene bis(4-fluorophenyl)methadone (mFDBP, 2), BDBF (3), dibenzo[b,d]thiophen-2-yl(4-fluorophenyl)methadone (FBDBT, 4), and ClBCZ (5). Their photophysical properties were systematically investigated in different states. These molecules were found to be non-luminescent in the solution and amorphous states but strongly emissive in the crystalline phase in ambient conditions. This suggests that crystallization induced RTP in these molecules, which is commonly observed in luminogens with aggregation-induced emission characteristics.
As a proof of concept, we describe BDBF as a representative for discussion. As suggested by the powder X-ray diffraction (PXRD) shown in Figure S2A, the BDBF powder obtained by two rounds of recrystallization from dichloromethane and hexane was crystalline, whereas the one obtained by heating the powder with a heating gun and then quenching the melt with liquid nitrogen was amorphous. Analysis of the time-resolved excitation and emission spectra given in Figures S2B and S2C revealed that the best excitation and emission wavelengths for BDBF for achieving efficient and persistent RTP are 350–400 and 550 nm, respectively.

Thus, when the crystalline BDBF powder was irradiated with 365 nm UV light at 300 and 77 K in air, intense green emission was observed. In contrast, its solution and amorphous powder emitted only at 77 K (Figure 5A). The steady-state photoluminescence (PL) spectra of the crystalline powder measured in air and in an inert atmosphere were almost identical, revealing that crystallization is an effective rigidification tool for triggering RTP by blocking emission quenching by oxygen and other nonradiative-decay pathways (Figure S2B). On the other hand, the phosphorescence feature of BDBF was intrinsic because of the large similarity between the PL spectrum and lifetime-decay curve at different states at 77 K (Figure 5B). In another experiment, we investigated the temperature effect on the PL of BDBF. With an increase in the temperature from 50 to 350 K, the emission of BDBF became weaker, probably because excited states have a higher probability of relaxing through non-radiative channels at elevated temperatures (Figure 5C). The time-resolved PL-decay curves of the crystalline powder measured at different wavelengths at 50 K demonstrate the pure phosphorescence characteristics of the luminescence. The photographs taken of the crystalline, solution, and amorphous samples in the presence and absence of the excitation source at 77 K and their associated spectra of prompt and delayed PL also suggest a similar idea (Figure S3). After removal of the excitation source, the emission faded slowly and could be followed by the naked eye (Figure 3D inset). The measured and calculated luminescence lifetimes at 300 K were the same and equal to 0.23 s, which is quite long among the reported RTP systems. The emission was strong with a \( \Phi_p \) of 34.5% in ambient conditions. On careful examination of the PL spectra and decay curves, we found the presence of two
emitting species with different overlapping emission spectra and lifetimes. As a result, the spectra of prompt and delayed PL at 77 K were similar but not exactly the same; they showed slightly difference peaks, and the spectrum of delayed PL included a tail (Figures 5B and S3). On further analysis of the decay curves, two-component (exponential) decays were seen to coexist in each emission band (Figure 5C, inset, and Table S1). Emission at shorter wavelengths consisted of faster decay and was quite sensitive to temperature. With decreasing temperature, emission at shorter wavelengths was greatly enhanced and became the dominant profile.

Similarly, the crystalline and amorphous samples of pDBP (1), mFDBP (2), FBDBT (4), and CIBCZ (5) were prepared and analyzed by PXRD (Figure S4). Similar to BDBF, these molecules exhibited bright phosphorescence in solutions (Figure S5) and amorphous states (Figure S6) at 77 K and stronger emission in the crystalline states (Figure S7) at low temperatures. As mentioned above, the π-extended units exerted a strong influence on the electronic properties or the emission behaviors of the
luminogens. As shown in Figure 6A, changing the aryl group varied the energy gap between T₁ and S₀, which changed the emission color of the molecules from blue to green to yellow, and even to orange-red. The lifetimes of most of the molecules were in hundreds of milliseconds, demonstrating the persistent nature of their emission (Figure 6B). In brief, pDBP (1) crystals emitted yellow light with a Φₚ of 6.8%, and the crystalline powders of mFDBP (2) showed a more intense green light with a higher Φₚ of 17.7%. On the other hand, FBDBT (4) crystals emitted pink light with a low Φₚ of 6.5%, but CIBCZ (5) crystals emitted an intense green light with the highest quantum yield of 36.0% and a shorter lifetime of 44 ms. The detailed lifetimes, quantum yields, and decay constants are summarized in Table S2. The nanosecond decay curves of the molecules and benzophenone are shown in Figure S8. No emission decay was detected in the nanosecond range, and all spectra coincided well with the spectrum in the absence of sample, demonstrating that the molecules synthesized in the present study are pure phosphors.

**DISCUSSION**

As revealed by our experimental data, we successfully achieved phosphors with tunable emission colors (from blue to orange-red), high efficiencies (up to 36.0%), and persistent lifetimes (up to 0.23 s) by using a proper π-conjugated system. Furthermore, we achieved persistent and efficient RTP achieved in a single molecule such as BDBF under ambient conditions. Although the performance was impressive, both the lifetime and efficiency were still lower than the best previously reported values. Careful examination of the performance of previous systems reveals a conflict. Generally, systems showing high efficiencies have short lifetimes in microseconds,²²,²³ whereas those with persistent lifetimes have low phosphorescence efficiencies.²⁶,²⁸ According to Equation 1, \( \Phi_p = \Phi_{ISC}(1-k_{ISC} \tau_p) \) shown in Figure 2B, using the same rigidification methodology suppresses \( k_{ISC} \) to almost the same level. Obviously, the increase in lifetime will simultaneously decrease the efficiency. On the one hand, a slow \( k_P \) (e.g., \( 10^{-3} \text{ s}^{-1} \) in Huang’s H-aggregation system²⁴) is needed for achieving a persistent lifetime but cannot easily compete with \( k_{ISC} \)' and will thus have a low efficiency. On the other hand, a high \( k_P \) will lead to a short lifetime but high...
efficiency as a result of the better competition with \( k_{ISC} \) (e.g., Kim’s halogen bonding system\(^{22,23}\)). As a result, endowing a persistent RTP system with high efficiency becomes more difficult than for systems with short lifetimes. If we can suppress \( k_{ISC} \) to an ignorable level (~0 s\(^{-1}\)), which is impossible, we could obtain RTP systems with both high efficiency and a persistent lifetime. However, this possibility is extremely challenging under ambient conditions. As a proof of concept, here we present a system with balanced performance in terms of efficiency and lifetime.

Figure 4B demonstrates the correlation between \( \beta_p \) and the measured \( \tau_P \) and calculated \( k_P \). The large dependence of \( \tau_P \) on \( \beta_p \) reveals that the molecular-orbital feature of \( T_1 \) determines the \( k_P \). A high \( \beta_p \) suggests a nearly pure \((\pi, \pi^*)\) characteristic of \( T_1 \), which shows a slow \( k_P \) and relaxes through a persistent phosphorescence-decay pathway. Importantly, the experimental results validate the molecular-orbital model and theoretical calculations, which can serve as an attractive endeavor for elucidating the fundamental structure-property relationship.

In summary, we present a clear picture for comprehensive understanding of the phosphorescence process of pure organic materials. The principle, which involves adjusting the characteristics of molecular orbitals and the exciton configuration in the excited state by varying the molecular structure, provides a tool for modulating the intrinsic RTP performance. Theoretical investigations on molecular orbitals reveal that the electronic configuration of the exciton is crucial to ISC and the decay of radiative phosphorescence. Thus, the molecular design of an excited state with hybrid configurations \((n, \pi^*)\) and \((\pi, \pi^*)\) in appreciable proportion is desired for obtaining efficient persistent RTP materials. By tuning the features of the molecular orbital and the energy level of the excited state through tailoring the aromatic subunits in arylphenones, we obtained a series of full-color pure organic phosphors with an efficiency of up to 36.0% and a long lifetime of 0.23 s under ambient conditions. The key issue is the synergistic effect of aromatic subunits and ketones, which realizes remarkably fast \( k_{ISC} \) and slow \( k_P \) to afford balanced performance. The rational guidelines gained from our experimental and theoretical investigations will allow for the exploration of novel organic phosphors.

**EXPERIMENTAL PROCEDURES**

All chemicals and other reagents were purchased from Aldrich and used as received without further purification. All molecules synthesized were purified by column chromatography, recrystallized twice from dichloromethane and hexane, and fully characterized by \(^1\)H nuclear magnetic resonance (NMR), \(^{13}\)C NMR, high-resolution mass spectroscopy, and elemental analysis. The photoluminescence spectra were measured on a PerkinElmer LS 55 spectrophotometer. The lifetime, time-resolved excitation spectra, steady-state and time-resolved emission spectra, temperature-dependent photoluminescence spectra, and absolute luminescence quantum yield were measured on an Edinburgh FLSP920 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe900), a microsecond flash lamp (uF900), a picosecond pulsed diode laser (EPL-375), a closed-cycle cryostate (CS202*-DMX-155, Advanced Research Systems), and an integrating sphere (0.1 nm step size, 0.3 s integration time, five repeats), respectively. Mean decay times \( \tau_D \) were obtained from individual lifetimes \( \tau_i \) and amplitudes \( a_i \) of multi-exponential evaluations. PXRD patterns were performed on an X’Pert PRO MPD diffractometer with Cu Kα radiation (\( \lambda = 1.5418 \) Å) at 25°C (scan range: 4.5°–50°). Single-crystal data were collected on a Bruker Smart APEXII CCD diffractometer using graphite-monochromated Cu Kα radiation (\( \lambda = 1.54178 \) Å). Photos
were recorded with a Canon EOS 60D. The DFT and TD-DFT calculations were performed with a Gaussian 09 program.

SUPPLEMENTAL INFORMATION
Supplemental Information includes Supplemental Experimental Procedures, 14 figures, and 5 tables and can be found with this article online at http://dx.doi.org/10.1016/j.chempr.2016.08.010.

AUTHOR CONTRIBUTIONS
W.Z. synthesized all materials and performed all photophysical measurements. Z.H. and W.Z. grew the crystals, analyzed the data, and prepared the paper. W.Z. and Z.H. contributed equally to this work. H.M., Z.S., and Q.P. performed the theoretical calculations. G.B. and J.H. assisted with measuring photophysical properties. J.W.Y.L. and B.Z.T. designed and supervised the research and wrote the paper. All authors discussed the results and commented on the manuscript.

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