Stabilizing triplet excited states for ultralong organic phosphorescence

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The control of the emission properties of synthetic organic molecules through molecular design has led to the development of high-performance optoelectronic devices with tunable emission colours, high quantum efficiencies and efficient energy/charge transfer processes4–9. However, the task of generating excited states with long lifetimes has been met with limited success, owing to the ultrafast deactivation of the highly active excited states6. Here, we present a design rule that can be used to tune the emission lifetime of a wide range of luminescent organic molecules, based on effective stabilization of triplet excited states through strong coupling in H-aggregated molecules. Our experimental data revealed that luminescence lifetimes up to 1.35 s, which are several orders of magnitude longer than those of conventional organic fluorophores10,11, can be realized under ambient conditions. These results outline a fundamental principle to design organic molecules with extended lifetimes of excited states, providing a major step forward in expanding the scope of organic phosphorescence applications.

Organic molecules with long-lived excited states enable exciton migration over long distances for increased production of free charges, which is essential for a variety of optoelectronic applications such as photovoltaics, photocatalytic reactions and molecular sensing12–15. As an added benefit, these organic molecules can be used as ideal contrast agents for high-sensitivity bioimaging as they allow elimination of short-lived background fluorescence16. Afterglow or persistent luminescence, which can last for an appreciable time from seconds to several days after the removal of the excitation source, has aroused particular attention due to its ultralong-lived excited state17. However, the afterglow phosphors are typically limited to metal-containing inorganic materials18, particularly rare-earth phosphors in which the emission is governed by slow liberation of trapped charge carriers from isolated traps of impurities, defects or ions through thermal stimulation with low luminescence efficiency19 (Fig. 1a). In contrast, long-lived excited states recorded for organic materials at room temperature generally involve the conversion of the spin-allowed short-lived (nanoseconds) singlet excited states to the spin-forbidden long-lived (microseconds) triplet excited states20. However, to enhance the transition of singlet-to-triplet states, either inorganic metals21 (for example, Ir^3+ and Pt^2+) or special organic moieties22 (for example, aromatic aldehyde, heavy halogen and deuterated carbon) are required. In addition, stringent conditions associated with inert atmospheres, carefully chosen hosts, rigid crystalline solid-state structures or ultralow temperatures are needed as

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Figure 1 | Schematic representation of the manipulation of the lifetime of excited states in inorganic and organic materials. a, Typical mechanism of afterglow luminescence in rare-earth-doped inorganic crystals where the luminescence of the emitters is persistently powered through thermal release (kT) of the charge carriers trapped at crystal lattice defects. b, Proposed mechanism for ultralong organic phosphorescence by constructing lower-lying energy states to stabilize the lowest triplet excited state (T1). Note that the fluorescence with short lifetimes of several nanoseconds on excitation (step 1) results from radiative deactivation of the molecule from the lowest singlet excited state (S1) to the ground state (S0). This excited molecule at S1 may also transform to T1 through intersystem crossing (step 2), enabling phosphorescence with typical lifetimes ranging from microseconds to milliseconds at room temperature. The stabilization of the excited molecules at T1 through H-aggregation (step 3) may lead to a newly formed triplet excited state (T1*) at a lower energy level, thus increasing the lifetime of phosphorescence (step 4). c, Rational design of the organic molecules used for the tuning of the lifetime of excited states. The incorporation of N, O and P atoms with lone-pair electrons aims to promote the production of the triplet excitons through n–π^* transition. The alkyl or aromatic substituents are introduced to support the formation of H-aggregates to stabilize the triplet excitons.
the triplet excitons generated in organic molecules are highly sensitive to oxygen and temperature. Inspired by the trapping of charge carriers for long-lived afterglow luminescence in inorganic materials, we reasoned that the formation of a largely emission-forbidden energy trap state (\(T^*\)) in organic molecules, analogous to the charge trapping centre in inorganic phosphors, may stabilize the triplet excited states of metal-free organic molecules in pursuit of long-lived excitons for ultralong phosphorescence at room temperature (Fig. 1b). Importantly, our approach may provide a much needed solution for achieving ultralong excited states in organic molecules under ambient conditions.

To validate our hypothesis, we designed and synthesized three types of purely organic molecule containing O, N and P atoms (Fig. 1c). Notably, these atoms favour the spin–orbit transition and hence facilitate the spin-forbidden transition of singlet-to-triplet excited states through intersystem crossing to populate triplet excitons. Another important element of molecular design is the inclusion of substituents that facilitate the formation of stable H-aggregates. The packing of the molecules by H-aggregation is known to increase the lifetime of singlet excited states through intersystem crossing to populate triplet excitons.

Fig. 2 | Investigation of the photoluminescence of a nitrogen-based model molecule (DPhCzT) under ambient conditions. a, Steady-state photoluminescence (steady-state PL, red line) and ultralong phosphorescence (ultralong phos., blue line) spectra of the DPhCzT molecules. Insets show the photographs of the DPhCzT powder under the two conditions. The spectra and photographs for the steady-state PL and the ultralong phosphorescence were recorded at 300 K on excitation at 365 nm and removal of the ultraviolet lamp, respectively. The upper inset shows a transient photoluminescence decay image of the sample recorded at 300 K. The colour change from red to green indicates the decrease in emission intensity. b, Steady-state photoluminescence spectra of the DPhCzT molecules measured at temperatures from 12 to 300 K. c, Time-resolved excitation spectra obtained at 300 K by monitoring the emission of the sample at 530 nm on varying the excitation wavelengths from 270 to 450 nm. d, Time-dependent luminescence decay of the ultralong phosphorescence of the sample recorded after excitation for 10 min with different light sources (254 or 365 nm ultraviolet light and simulated sunlight; 1,000 ± 5% lx). e, Top: Intensity profile of the 530 nm ultralong phosphorescence as a function of time on excitation at 365 nm. Bottom: Time-dependent intensity scan of the 530 nm emission obtained with an excitation interval of 2 s. f, Lifetimes of the 530 nm emission recorded for samples dispersed in THF containing different amounts of water. The wavelength of excitation is at 320 nm. Inset: Photographs of representative photoluminescence (left) and ultralong phosphorescence (right) of the samples dispersed in THF/H\(\text{H}_2\text{O}\) (20/80 vol/vol) at 300 K under excitation at 365 nm and after the removal of the light source, respectively.

The resolved emission bands at 530 and 575 nm with single exponential decays are characteristics of the ultralong-lived luminescence (Supplementary Fig. 1d) with an absolute quantum efficiency of ~1.25% (Supplementary Table 2). In addition, almost identical steady-state photoluminescence spectra and lifetime measurements of the DPhCzT molecules in solid state were obtained in different media (oxygen, argon and ambient atmosphere), revealing an insensitivity to oxygen (Supplementary Fig. 6).

In a further set of experiments, we investigated the effects of temperature on the photoluminescence of DPhCzT. On decreasing the temperature from 300 to 12 K, the emission intensity and lifetime of DPhCzT increased, but the quantum efficiency of the ultralong emission remained essentially the same as a result of its insensitivity towards the low temperature (Supplementary Fig. 6). However, on increasing the temperature from 303 to 423 K, the ultralong luminescence at 530 and 575 nm decreased gradually and disappeared at 383 K, but recovered when the temperature was lowered to 363 K (Supplementary Fig. 7b,c). The X-ray diffraction patterns of DPhCzT powder show negligible changes in molecular packing at elevated temperatures from 298 to 423 K (Supplementary Fig. 8). Taken together, these data suggest that the enhanced non-radiative transition of the excited states at elevated temperatures is likely to be the main cause for the suppression of the ultralong luminescence.

Time-resolved excitation spectroscopy studies revealed that the ultralong phosphorescence emission of DPhCzT at 530 nm can
be efficiently excited within the range of 270 to 420 nm (Fig. 2c). Critically, the powdered sample gave rise to the longest decay time (1.06 s) when irradiated at around 362 nm. The absolute luminescence of the sample, excited under ultraviolet (254 and 365 nm) and simulated sunlight at room temperature, remains at about 53, 61 and 134 mcd cm\(^{-2}\) s\(^{-1}\) at a delay time of 1 s (Fig. 2d). Impressively, this ultralong phosphorescence can be effectively activated by a relatively low power of excitation (<50 \(\mu W \text{cm}^{-2}\)) within a short period of time (<0.6 s) under ambient conditions (Supplementary Figs 9 and 10). The resistance of the ultralong organic luminescence to photobleaching was further confirmed by repeated excitation cycles of more than 100 times (Fig. 2e and Supplementary Fig. 10c). It should be noted that DPhCzT molecules dispersed in a mixed solution of tetrahydrofuran (THF) and water can also exhibit long-lived luminescence (>0.46 s; Fig. 2f).

To probe the mechanism of the observed ultralong luminescence from pure organic compounds, we performed first-principles time-dependent density functional theory (TD-DFT) investigations on single molecules and aggregated structures in both singlet and triplet excited states\(^{14}\). The calculated energy levels of a DPhCzT monomer at the lowest singlet \(E_{S_0} = 3.43 \text{ eV}\) and triplet \(E_{T_1} = 3.14 \text{ eV}\) excited states are considerably close (≤0.3 eV), which enables the facilitation of single–triplet intersystem crossing processes\(^2\) (Fig. 3a). Furthermore, the transition configurations and isosurfaces of \(S_1\) and other triplet excited states \((T_2, T_3, T_4)\) of 3.38 Å, corresponding to the packing distance obtained in a single crystal.
and T<sub>4</sub>) are quite similar (Fig. 3a and Supplementary Table 4), thereby enhancing the spin–orbit coupling probability and thus the intersystem crossing process<sup>2</sup>. Theoretically, for isolated DPhCzT monomers there are four main transitions from S<sub>1</sub> to T<sub>n</sub> (S<sub>1</sub>→T<sub>1</sub>, T<sub>1</sub>, T<sub>4</sub>, and T<sub>4</sub>) for intersystem crossing. However, our calculations, derived from a single-crystal structure containing an aggregated DPhCzT dimer, support enhanced intersystem crossing due to an increased number of energy transition channels (S<sub>1</sub>→T<sub>1</sub>, T<sub>1</sub>, T<sub>4</sub>, T<sub>4</sub>, and T<sub>4</sub>) for intersystem crossing (Fig. 3b and Supplementary Figs 13 and 14 and Supplementary Tables 5–7).

The existence of triplet states in aggregated DPhCzT molecules was experimentally confirmed by photodegradation of anthracene-9,10-diyl-bis-methylmalonate (ADMA) in the presence of DPhCzT and molecular oxygen<sup>19</sup>. The characteristic absorbance (358, 378 and 399 nm) of ADMA dispersed in THF or THF/H<sub>2</sub>O (20/80; v/v) solutions gradually decreases with prolonged illuminated time (Fig. 3c), indicating the formation of triplet excited states on photoexcitation. Furthermore, on the basis of single-crystal X-ray diffraction analysis, the angle between transition dipoles and the interconnected axis (θ) is larger than the critical value of 54.7°, manifesting the presence of H-aggregates<sup>27</sup> (Fig. 3d,e). The formation of H-aggregates was further confirmed by gradual emergence of a blueshifted absorption peak around 320 nm when increasing the H<sub>2</sub>O content from 1% to 20% in a methanol solution of DPhCzT (Supplementary Fig. 18).

The key to populating triplet states is the enhancement of spin–orbit coupling through n→π* transition for improved intersystem crossing<sup>28</sup>. The DPhCzT molecule is ideal in this regard because its constituting nitrogen atoms promote the n→π* transition. Considering that the H-aggregates support the molecular equivalent of an indirect exciton with increased excited-state lifetimes, we reasoned that the strong coupling in π→π* stacking of the triazine-based compounds in the form of H-aggregation with considerably large transition dipole moment (Supplementary Table 16) provides an effective means of stabilizing and protecting the triplet excitons formed through intersystem crossing (Fig. 3f). The stabilized excited state (T<sub>4</sub>*), which functions as an energy trap at a lower energy level, may delocalize on several neighbouring molecules<sup>29</sup>, offering suppressed radiative and non-radiative deactivation decay rates in favour of long-lived excited states and ultralong phosphorescence. To further validate this hypothesis, we calculated distance-dependent binding energy in a DPhCzT dimer at the lowest triplet state<sup>30</sup>. By fitting with a Lennard-Jones model, the stabilizing energy (ε) of the DPhCzT dimer was estimated to be 0.98 eV (Fig. 3g). The binding energy of the DPhCzT dimer with a stacking distance of 3.38 Å reaches 0.77 eV, illustrating theoretical evidence for the substantial impact of H-aggregation on triplet excitons. The high exciton binding energies experimentally measured for both singlet and triplet states (0.25 and 0.26 eV, respectively) clearly suggest the Frenkel-like character of the excitons in H-aggregates.

To test the generality of our approach to achieving ultralong organic phosphorescence, we designed a series of organic molecules (DEOPh, DcZT, CzDClT and DCzPhP) containing O, N and P atoms capable of promoting spin-forbidden singlet–triplet
interstate crossing through \(n^\pi^*\) transition (Fig. 4a). Note that planar molecular structures with well-defined substituents are essential to induce parallel alignment of the molecules and thus the formation of H-aggregates\(^3\), which can stabilize the excited states and extend phosphorescence lifetime. As anticipated, these organic compounds all exhibited relatively long triplet lifetimes ranging from 0.21 to 1.35 s, resulting in a noticeable change in the glowing background of the compounds from one colour to another (Fig. 4a and Supplementary Figs 21 and 22). From these data, dynamic photophysical parameters of both fluorescence and ultralong phosphorescence were extrapolated (Supplementary Table 18). The radiative \((k_{\text{rad}}^n)\) and non-radiative decay \((k_{\text{nr}}^n)\) rates of the ultralong phosphorescence are 10\(^{6}\) times slower than those of the fluorescence owing to the spin-forbidden feature of the \(T_1 \rightarrow S_0\) transition. The intersystem crossing rates \((k_{\text{isc}})\) of these molecules are comparable to their corresponding radiative decay rates \((k_{\text{rad}}^n)\), indicating an efficient intersystem crossing process to produce sufficient triplet excitons responsible for the recordable ultralong phosphorescence. Notably, the existence of lower-lying emissive triplet states \((T_i)\) with low radiative \((k_{\text{rad}}^m \sim 10^{-1} \text{s}^{-1})\) and low non-radiative decay rates \((k_{\text{nr}}^m \sim 1 \text{s}^{-1})\) is the key to the ultralong phosphorescence with lifetimes up to seconds at room temperature.

The organic phosphors carrying distinguishable lifetime codes could be used in developing niche applications in document security (Fig. 4b). Although virtually invisible under ultraviolet light excitation because of the background fluorescence \((<3 \text{ ns})\) interference induced by a poly[9,9-diocytfluorene-co-2,2'-bis(octyloxy)-1,1'-binaphthyl] (PFB) dye molecule, the patterned sensitivity feature of 2014' encrypted with ultralong phosphorescent DPhCzT molecules could be readily visualized by switching off the excitation. In view of the inherent merits of light weight, flexibility, and mild synthetic conditions\(^2\), the organic materials with colourful ultralong phosphorescence may hold great promise for advanced optoelectronic applications requiring long-lived excited states.

In conclusion, we have presented a basic design principle for manipulating the excitation lifetime in organic materials. The principle, which involves the stabilization of the triplet excitons through molecular H-aggregation, provides convenient access to visible ultralong-lived luminescence \((>1 \text{ s})\) in a diverse array of purely organic molecules at room temperature. By tailoring the structure of the molecules, the colour of ultralong phosphorescence can be tuned from green \((515 \text{ nm})\) to red \((644 \text{ nm})\) under ambient conditions. The understanding gained from our experimental and theoretical investigations will allow for the construction of next-generation organic phosphors that may revolutionize the fields of organic optoelectronics, molecular imaging, storage encryption and data security.

**Methods**

Unless otherwise noted, all reagents were purchased from Aldrich and Acros and used without additional purification. The molecular structures of the as-synthesized phosphorescent molecules were fully characterized by single-crystal X-ray diffraction, NMR spectroscopy, mass spectrometry and element analysis (see Supplementary Information).

The steady-state ultraviolet absorption data and photoluminescence spectra were collected on a SHIMADZU UV-3600 ultraviolet-visible–near-infrared spectrophotometer and an RF-5301PC spectrofluorophotometer, respectively. The time-resolved excitation spectra, kinetic measurements, lifetime and time-resolved emission spectra were measured using an Edinburgh FLSP920 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe9900), a nanosecond hydrogen flash lamp (N9200) and a microsecond flash lamp (N9900), respectively. X-ray crystallography was carried out on a Bruker SMART APEX-II CCD diffractometer equipped with graphite monochromated Mo-K\(_\alpha\) radiation. The X-ray diffraction pattern was collected on a D/max-2500/PC diffractometer using Cu K\(_\alpha\) radiation (\(\lambda = 1.5405 \) A). The photos and supporting movies were recorded by a Nikon D90. The ultralong phosphorescence intensity was measured by a PR305 photometer after the sample was irradiated by either 254 or 365 nm ultraviolet light or a simulated sunlight excitation source with 1,000 ± 5% lx for 10 min. The TD-DFT calculations were performed with the Gaussian 09 program.


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Author contributions
Z.A., C.Z., Y.T., R.C., X.L. and W.H. conceived the experiments. R.C., X.L. and W.H. prepared the paper. Z.A., C.Z., Y.T. and H.S. were primarily responsible for the experiments. R.D., Z.W. and H.L. performed the lifetime measurements. T.C. contributed to TD-DFT calculations. All authors contributed to the data analyses.

Additional information
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Competing financial interests
The authors declare no competing financial interests.