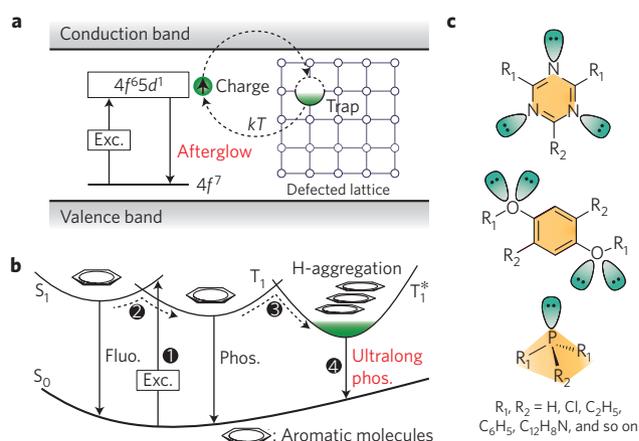


# Stabilizing triplet excited states for ultralong organic phosphorescence

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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 processes<sup>1–4</sup>. 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 states<sup>5</sup>. 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 fluorophores<sup>6,7</sup>, 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.

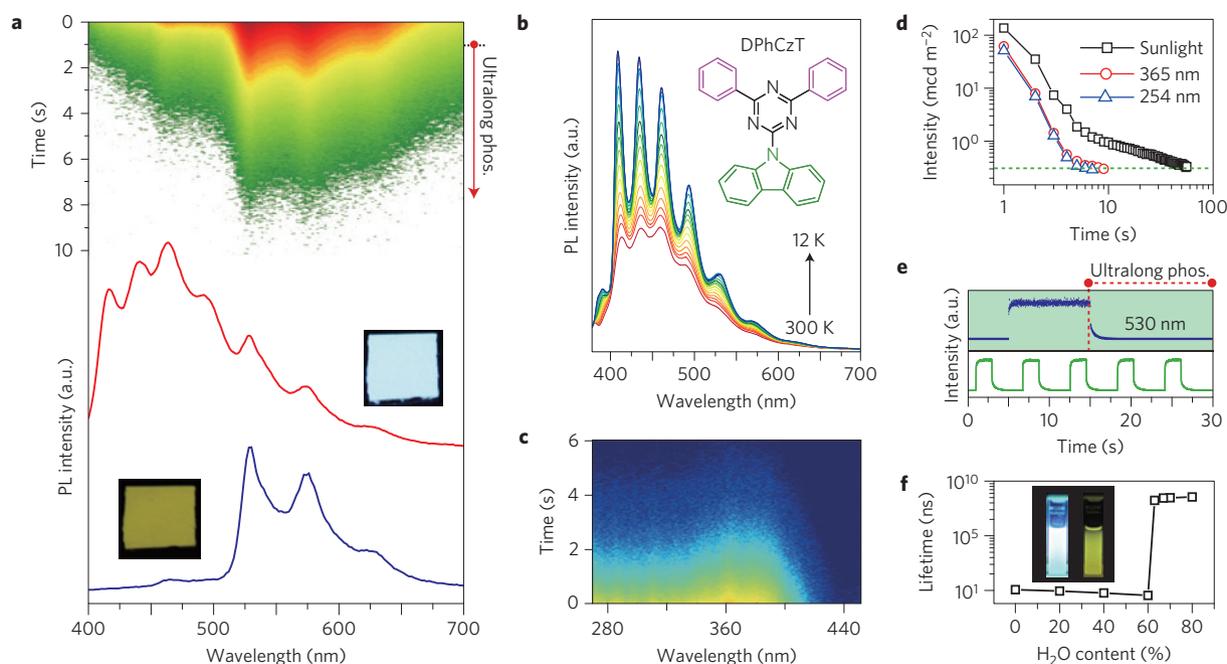
Organic molecules with long-lived excited states enable exciton migration over long distances for increased production of free charges, which is essential for a variety of optoelectronic applications such as photovoltaics, photocatalytic reactions and molecular sensing<sup>8–12</sup>. As an added benefit, these organic molecules can be used as ideal contrast agents for high-sensitivity bioimaging as they allow elimination of short-lived background fluorescence<sup>13</sup>. 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 state<sup>14</sup>. However, the afterglow phosphors are typically limited to metal-containing inorganic materials<sup>14</sup>, 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 efficiency<sup>15</sup> (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 states<sup>16</sup>. However, to enhance the transition of singlet-to-triplet states, either inorganic metals<sup>17</sup> (for example, Ir<sup>3+</sup> and Pt<sup>2+</sup>) or special organic moieties<sup>18</sup> (for example, aromatic aldehyde, heavy halogen and deuterated



**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 ( $T_1$ ). 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 ( $S_1$ ) to the ground state ( $S_0$ ). This excited molecule at  $S_1$  may also transform to  $T_1$  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  $T_1$  through H-aggregation (step 3) may lead to a newly formed triplet excited state ( $T_1^*$ ) 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  $n-\pi^*$  transition. The alkyl or aromatic substituents are introduced to support the formation of H-aggregates to stabilize the triplet excitons.

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 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;  $1,000 \pm 5\%$  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<sub>2</sub>O (20/80 vol/vol) at 300 K under excitation at 365 nm and after the removal of the light source, respectively.

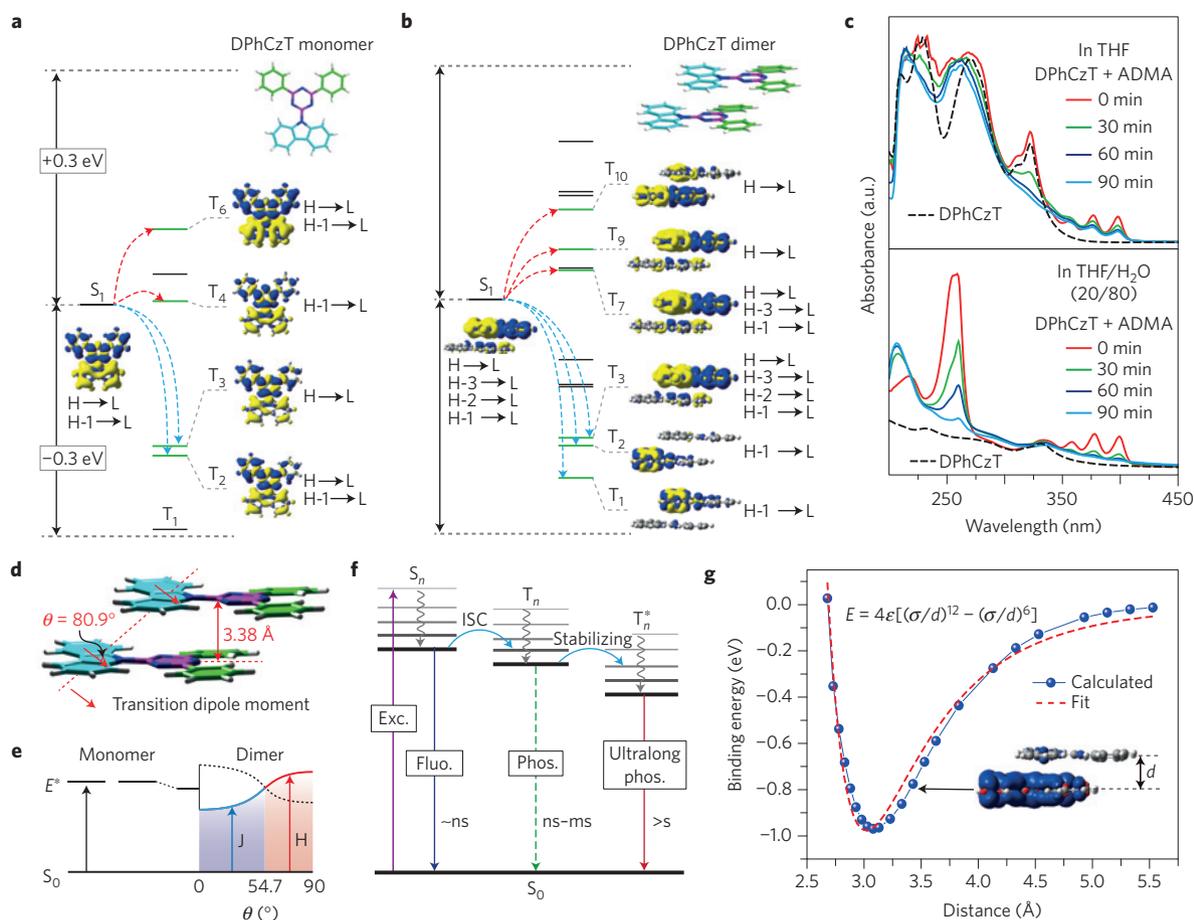
the triplet excitons generated in organic molecules are highly sensitive to oxygen and temperature<sup>19,20</sup>. Inspired by the trapping of charge carriers for long-lived afterglow luminescence in inorganic materials, we reasoned that the formation of a largely emission-forbidden energy trap state ( $T_1^*$ ) in organic molecules, analogous to the charge-trapping centre in inorganic phosphors<sup>14,21</sup>, 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  $n-\pi^*$  transition and hence facilitate the spin-forbidden transfer of singlet-to-triplet excited states through intersystem crossing to populate triplet excitons<sup>12</sup>. 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<sup>22,23</sup>. As a proof of principle, we synthesized 4,6-diphenyl-2-carbazolyl-1,3,5-triazine (DPhCzT) and systematically investigated its photoluminescence properties. On ultraviolet irradiation at 365 nm, an intense blue emission ranging from 400 to 500 nm peaks was observed from DPhCzT powder. Interestingly, on removal of the ultraviolet source the emission changed in colour and slowly faded with a remarkably long luminescence lifetime of 1.06 s (Fig. 2a). 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  $\sim 1.25\%$  (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 inertness of the triplet excited states to oxygen (Supplementary Fig. 1e–g and Supplementary Movie 1).

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<sup>22</sup>.

Time-resolved excitation spectroscopy studies revealed that the ultralong phosphorescence emission of DPhCzT at 530 nm can

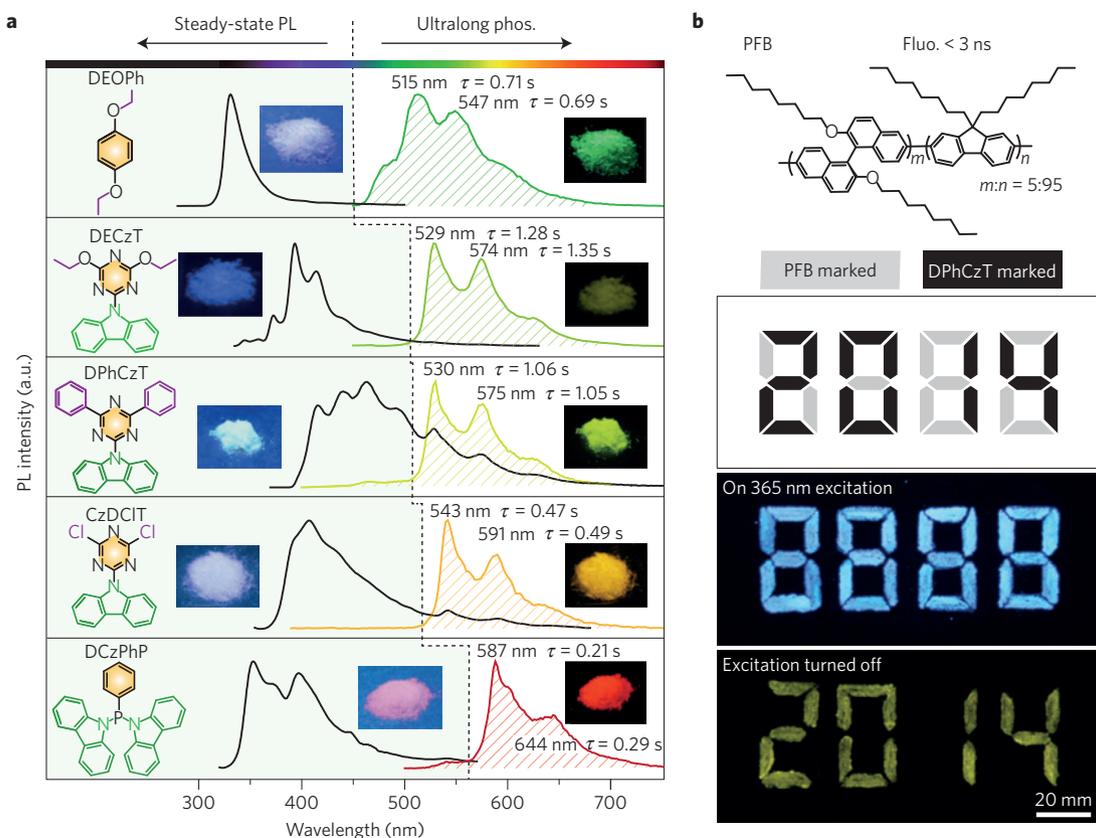


**Figure 3 | Proposed mechanism for ultralong phosphorescence of the DPhCzT aggregates.** **a, b**, Schematic diagrams showing the TD-DFT-calculated energy levels, isosurface and main orbital configurations of a DPhCzT monomer and its coplanar dimer at singlet ( $S_n$ ) and triplet ( $T_n$ ) states. Note that H and L refer to highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. The molecular packing in **b** is derived from single-crystal diffraction data. The red and blue dashed arrows in **a** and **b** represent the intersystem crossing processes probably occurring from the  $S_1$  state to its higher- or lower-lying triplet states ( $T_n$ ). The green lines refer to the triplet states available for effective intersystem crossing transitions. **c**, The absorption spectra of a DPhCzT and ADMA mixture dissolved in a THF/H<sub>2</sub>O (20/80) solution (20  $\mu$ M), confirming the presence of the triplet excited states in DPhCzT. The spectra were obtained by excitation of the solutions at 330 nm for 0, 30, 60 and 90 min, respectively. **d**, Single-crystal structures of DPhCzT showing the formation of H-aggregates as evident by the measured angle ( $\theta$ ) of 80.9° between the transition dipoles and interconnected axis. **e**, Schematic energy diagram of J-aggregation ( $\theta < 54.7^\circ$ ) and H-aggregation ( $\theta > 54.7^\circ$ ). The blue and red solid curves represent the exciton energy levels of allowed transition for J- and H-aggregation, respectively. The dotted curve refers to the corresponding exciton energy level of forbidden transition. **f**, Proposed energy transfer processes for fluorescence (Fluo.), phosphorescence (Phos.) and ultralong phosphorescence (Ultralong phos.) in DPhCzT aggregates. The  $n-\pi^*$  transition derived from nitrogen atoms in the conjugated heterocycle enhances spin-orbit coupling. This in turn populates triplet states through singlet-triplet intersystem crossing (ISC). The triplet excitons are quickly stabilized because of the H-aggregation of DPhCzT molecules, resulting in the formation of stabilized triplet excited states ( $T_n^*$ ) with extended lifetime needed for ultralong phosphorescence. The internal relaxation processes of the excitons are marked by grey wavy arrows. Dynamic photophysical parameters were measured and are listed in Supplementary Table 18. **g**, Calculated binding energy versus the molecular distance in the DPhCzT dimer ( $d$ ) at the lowest triplet state ( $T_1$ ). The data were fitted (red dashed curve) with a Lennard-Jones model to calculate the stabilizing energy ( $\epsilon = 0.98$  eV). Inset: Spin-density distribution of the dimer with a distance ( $d$ ) of 3.38 Å, corresponding to the packing distance obtained in a single crystal.

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 luminance 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<sup>-2</sup> 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 cm<sup>-2</sup>) 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<sup>24</sup>. The calculated energy levels of a DPhCzT monomer at the lowest singlet ( $E_{S_1} = 3.43$  eV) and triplet ( $E_{T_1} = 3.14$  eV) excited states are considerably close (<0.3 eV), which enables the facilitation of single-triplet intersystem crossing processes<sup>2</sup> (Fig. 3a). Furthermore, the transition configurations and isosurfaces of  $S_1$  and other triplet excited states ( $T_2$ ,  $T_3$ ,  $T_4$



**Figure 4 | Versatile molecular design for ultralong phosphorescence with tunable colours and data encryption application under ambient conditions.**

**a**, The steady-state photoluminescence (left) and ultralong phosphorescence (right) spectra of a series of specially designed molecules. Insets show the corresponding photographs taken before (left) and after (right) the excitation source is turned off. Note that the compound of DEOPh is excited at 254 nm at 300 K, whereas the other four compounds are excited at 365 nm at 300 K. **b**, Demonstration of lifetime-encoding for security application using DPhCzT in combination with a PFB dye molecule. On excitation at 365 nm with an ultraviolet lamp, the patterned security feature is unrecognizable owing to the background fluorescence of the PFB dye. The encrypted feature of '2014' made with ultralong phosphorescent DPhCzT molecules can be unmistakably identified by the naked eye after the excitation is switched off.

and  $T_6$ ) are quite similar (Fig. 3a and Supplementary Table 4), thereby enhancing the spin-orbit coupling probability and thus the intersystem crossing process<sup>25</sup>. Theoretically, for isolated DPhCzT monomers there are four main transitions from  $S_1$  to  $T_n$  ( $S_1 \rightarrow T_2$ ,  $T_3$ ,  $T_4$  and  $T_6$ ) 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 ( $S_1 \rightarrow T_1$ ,  $T_2$ ,  $T_3$ ,  $T_7$ ,  $T_9$  and  $T_{10}$ ; 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>26</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 ( $\theta$ ) 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  $n-\pi^*$  transition for improved intersystem

crossing<sup>28</sup>. The DPhCzT molecule is ideal in this regard because its constituting nitrogen atoms promote the  $n-\pi^*$  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  $\pi-\pi$  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 ( $T_1^*$ ), 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 ( $\epsilon$ ) 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, DECzT, CzDCIT and DCzPhP) containing O, N and P atoms capable of promoting spin-forbidden singlet-triplet

intersystem crossing through  $n-\pi^*$  transition<sup>29</sup> (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<sup>31</sup>, 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 ( $k_r^{\text{Phos}}$ ) and non-radiative decay ( $k_{nr}^{\text{Phos}}$ ) rates of the ultralong phosphorescence are  $10^8$  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 ( $k_{isc}$ ) of these molecules are comparable to their corresponding radiative decay rates ( $k_r^{\text{Fluo}}$ ), 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 ( $T_1^*$ ) with low radiative ( $k_r^{\text{Phos}} \sim 10^{-3} \text{ s}^{-1}$ ) and low non-radiative decay rates ( $k_{nr}^{\text{Phos}} \sim 1 \text{ s}^{-1}$ ) 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 ns) interference induced by a poly[9,9-dioctylfluorene-co-2,2'-bis(octyloxy)-1,1'-binaphthyl] (PFB) dye molecule, the patterned security 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<sup>32</sup>, 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 exciton 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 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 nm) to red (644 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 (Xe900), a nanosecond hydrogen flash-lamp (nF920) and a microsecond flash-lamp (uF900), 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 ( $\lambda = 1.5405 \text{ \AA}$ ). 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  $1,000 \pm 5\%$  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.