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Anion-regulated transient and persistent phosphorescence and size-dependent ultralong afterglow of organic ionic crystals

Anion-regulating transient and persistent phosphorescence and size-dependent ultralong afterglow of organic ionic crystals are demonstrated by alteration of anion and crystal size.

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### Introduction

Organic materials that exhibit room-temperature phosphorescence have been emerging as a promising alternative to long-lived phosphorescent inorganic and organometallic counterparts widely applied in energy and life sciences.<sup>1</sup> Although great advances in discovering and designing organic molecules with roomtemperature phosphorescence have been made recently,<sup>2</sup> it is still a formidable challenge to achieve efficient organic phosphorescence because of the following two major obstacles. The inherent long-lived emission of phosphorescence makes the generated triplet excitons to be readily consumed by the surroundings like oxygen. To overcome this problem, diverse approaches, such as polymer embedding,<sup>3</sup> crystallization<sup>4</sup> and host–guest capsulation,<sup>5</sup> have been proposed to effectively protect triplet excitons by constraining molecular motion and

# Anion-regulated transient and persistent phosphorescence and size-dependent ultralong afterglow of organic ionic crystals<sup>†</sup>

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It is a formidable challenge to achieve highly efficient organic afterglow and readily tunable transient and persistent phosphorescence of organic materials because of the lack of valid design principles. Herein, we report the regulation of the transient and persistent room-temperature phosphorescence of organic ionic crystals by the alteration of anions, and the unique size-dependent ultralong afterglow of tetraphenylphosphonium perchlorate (TPP  $ClO_4$ ) crystals under ambient conditions. Three organic ionic crystals show sharply distinct triplet emissions based on three heavy-atom free anions by proper construction of donor–acceptor patterns in the crystals. TPP  $ClO_4$  crystals exhibit ultrabright transient phosphorescence and ultralong afterglow, and the gradual enhancement of the afterglow with the crystal size directly proves the generation of ultralong afterglow from aggregates with strong intermolecular interactions in the crystals. These results greatly contribute to the general design principles of highly efficient transient and persistent phosphorescence and their regulations by rational design. Highly sensitive detection and imaging of perchlorate ions are achieved in a phosphorescence turn-on manner based on the bright room-temperature phosphorescence of TPP  $ClO_4$  crystals, and valuable anti-counterfeiting applications of the ultralong afterglow of TPP  $ClO_4$  crystals are also demonstrated in practical examples.

> intramolecular vibration and rotation.<sup>6</sup> However, to achieve highly efficient room-temperature phosphorescence, another obstacle regulated by the general principle that electronic transitions from excited singlet states to triplet states are forbidden should be properly handled. There are two dominant ways to promote intersystem crossing processes between singlet and triplet states currently. One of them is to introduce heavy atoms like bromine into luminogens to enhance the promotion from singlet to triplet states due to the spin-orbit coupling effect of the heavy atoms,<sup>7</sup> while the other means is to boost the population of triplet excitons by tuning the energy level via the introduction of particular functional groups like carbonyl and nitro groups8 or mixing appropriate electron donor and electron acceptor pairs.9 In comparison with the former approach relying on the heavy atom effect, rational design of luminogens of donoracceptor type is more promising to achieve diverse and highly phosphorescent organic materials from the few examples with extraordinary emission efficiency (>0.4) reported in the literature.4a,8a,10

> Persistent phosphorescence referring to the emission that can last for more than several seconds after ceasing the excitation frequently takes place along with transient room-temperature phosphorescence on the microsecond timescale.<sup>11</sup> Such a long-lived afterglow has indispensible advantages in time-gated luminescence imaging and anti-counterfeiting areas relative to transient

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#### Paper

phosphorescence due to its time-dimensional resolution by the naked eye.<sup>12</sup> A variety of organic crystals with ultralong afterglow have been discovered and designed, but its exact generation mechanism is still an open question because of the lack of direct and solid evidence. Recent studies have revealed that the generation of persistent phosphorescence is probably associated with the formation of H-aggregates<sup>13</sup> and strong intermolecular interaction or electronic coupling<sup>14</sup> in the crystals. However, there are only very few examples that exhibit both ultra-bright and ultralong afterglow because of the unclear generation mechanism and design principles of afterglow.15 Our recent study showed that significant intermolecular electronic coupling among molecules in the crystal causes the occurrence of persistent phosphorescence, and the introduction of heavy bromine atoms is capable of appreciably enhancing the emission efficiency, but its lifetime is largely shortened to a transient phosphorescence.<sup>16</sup> Therefore, a further exploration of the influence of crystal engineering and structural design on organic afterglow will greatly contribute to the general principles of achieving highly efficient ultralong phosphorescence in organic materials.<sup>17</sup>

In contrast to ordinary organic crystals consisting of neutral molecules, organic ionic crystals always retain their ordered crystal packing and can exhibit bright room-temperature phosphorescence through rational design,<sup>18</sup> and thus are a class of desirable platforms to investigate the generation mechanism of persistent phosphorescence. In this work, we report anionregulated transient and persistent phosphorescence based on tetraphenylphosphonium (TPP) cations and unique size-dependent afterglow of tetraphenylphosphonium perchlorate (TPP ClO<sub>4</sub>) crystals. As shown in Scheme 1, three TPP crystals show sharply distinct luminescence behaviours relying on the diversity of anions, and only TPP ClO<sub>4</sub> crystals exhibit highly efficient transient blue phosphorescence and bright green afterglow with a long emission time of 4 s. The underlying mechanisms for the enhancement of both transient and persistent phosphorescence are investigated by crystal structure analysis and theoretical computations. It is more



Scheme 1 Schematic illustration of anion-regulated transient and persistent phosphorescence (a) and size-dependent afterglow of tetraphenyl-phosphonium perchlorate crystals (b).

important to discover the unique size-dependent behaviour of the ultralong afterglow of TPP  $ClO_4$  crystals, and such direct and solid proof clearly substantiates the aggregate-based photophysical properties for ultralong afterglow. The ultrahigh quantum yield of the transient blue phosphorescence of TPP  $ClO_4$  microcrystals allows us to establish an ultrasensitive detection method for perchlorate ions in aqueous solution and on solid-substrates, and a further *in vivo* imaging study of seedlings of *Arabidopsis thaliana* validates its practicability in complex matrices. The distinguishable afterglow of TPP  $ClO_4$  by the naked eye is demonstrated in the time-dimensional anti-counterfeiting of a school badge and a banknote.

### **Results and discussion**

# Synthesis and characterization of tetraphenylphosphonium tetrafluoroborate (TPP BF<sub>4</sub>) and tetraphenylphosphonium perchlorate (TPP ClO<sub>4</sub>)

Tetraphenylphosphonium tetrafluoroborate (TPP BF<sub>4</sub>) and tetraphenylphosphonium perchlorate (TPP ClO<sub>4</sub>) were synthesized by precipitating reactions of tetraphenylphosphonium chloride (TPP Cl) with NaBF<sub>4</sub> and NaClO<sub>4</sub>, respectively. TPP Cl, TPP BF<sub>4</sub> and TPP ClO<sub>4</sub> were purified by multiple recrystallization, and fully characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>31</sup>P NMR, <sup>19</sup>F NMR and high-resolution mass spectrometry. The purities of these crystals were further verified using high-performance liquid chromatography. The HPLC results in Fig. S1 (ESI<sup>†</sup>) show that the purities of TPP Cl, TPP BF<sub>4</sub> and TPP ClO<sub>4</sub> were satisfactory (>99.0%), excluding the possibility of intense luminescence from impurities included in the crystals. Their structures were determined using single-crystal X-ray diffraction and are displayed in Fig. S2 (ESI<sup>†</sup>), which gave their absolute structural configurations and ionic arrangements for theoretical analysis.

# Distinct photophysical behaviours of TPP Cl, TPP $\mathsf{BF}_4$ and TPP $\mathsf{ClO}_4$ crystals

The three tetraphenylphosphonium compounds showed completely different luminescent behaviours depending on diverse anions. TPP Cl crystals exhibited a very weak green emission located at 500 nm with an ultralong lifetime of 253.2 ms, and their observable afterglow can last for a short period of 1.5 s (Fig. S3, ESI<sup>†</sup>).<sup>18b</sup> The TPP BF<sub>4</sub> crystals emit intense blue light under UV light irradiation, and the emission maximum is located at 430 nm (Fig. 1a). After 5.0 ms decay time is applied, a new weak green emission is detected at 490 nm (Fig. 1b), indicating that TPP BF4 exhibits an ultralong luminescence like TPP Cl. As shown in Fig. 1c, the bright blue emission quickly disappears after ceasing the excitation, and a faint green afterglow of up to 1.5 s can be observed by the naked eye. The timeresolved PL decay curves in Fig. S4 (ESI<sup>+</sup>) show that the lifetime at 420 nm is 4.5 µs, but the lifetime of one component is as long as 272.6 ms, indicating its ultralong afterglow of 1.5 s. In contrast to TPP Cl, TPP BF4 simultaneously exhibits two emissions including a strong ordinary room-temperature phosphorescence and a weak ultralong afterglow lasting for a few seconds.



Fig. 1 (a) PL spectra of TPP  $BF_4$  crystals, (b) time-gated PL spectra of TPP  $BF_4$  crystals and (c) ultralong afterglow of TPP  $BF_4$  crystals.

The phosphorescence quantum yield of TPP BF<sub>4</sub> crystals was determined to be as high as 0.48, which is much higher than those of most reported organic phosphors.<sup>2</sup> It is surprisingly found that an intense blue room-temperature phosphorescence and a strong green ultralong afterglow occurred simultaneously for TPP  $ClO_4$  crystals. Two separate emissions with equivalent PL intensity located at 420 nm and 475 nm were recorded for TPP  $ClO_4$  crystals (Fig. 2a), and the PL spectra at different decay times from 1.0 to 4.5 s clearly suggest that an intense and broad emission centered at 500 nm can last for 4 s after stopping the excitation light (Fig. 2b). The time-resolved PL decay curve at 420 nm shows that this emission has a relatively short lifetime of 2.8  $\mu$ s, and such a lifetime on the microsecond timescale illustrates that it comes from triplet



Fig. 2 (a) PL spectra of TPP ClO<sub>4</sub> crystals, (b) PL spectra of TPP ClO<sub>4</sub> crystals at different decay times from 1.0 to 4.5 s, (c) time-resolved PL decay curve at 420 nm, (d) time-resolved PL decay curve at 475 nm, and (e) ultralong afterglow of TPP ClO<sub>4</sub> crystals.

emission (Fig. 2c). It is noted that the emission at 475 nm originated from two major components, and the lifetime of the longer-emitting component is nearly 1 s (952.6 ms) from its decay curve (Fig. 2d). The ultra-high brightness of the blue phosphorescence can be readily observed by the naked eye when TPP ClO<sub>4</sub> crystals are irradiated with UV light, and the green afterglow also was almost as intense as the blue emission and persisted for more than 4 s after ceasing the excitation (Fig. 2e). In comparison with TPP Cl and TPP BF4, both the room-temperature phosphorescence and ultralong afterglow of TPP ClO<sub>4</sub> crystals have appreciably high emission efficiencies, and their total quantum yield is as high as 0.56 determined by an absolute method (Table S1, ESI†). Their quantum yield for transient phosphorescence is just only inferior to those of 1,4-dibenzoyl-2,5-bis(siloxy)-benzenes (0.64)<sup>4a</sup> and 1,2,3,4,5,6-hexakis(arylthio)-benzenes (1.0)<sup>10a</sup> without afterglow, and their efficiency for persistent phosphorescence is the highest compared to those for previously reported ultralong organic phosphorescence emissions (<0.345).<sup>8a</sup> It is also the first example with equivalently bright transient and persistent phosphorescence to the best of our knowledge. The aggregationinduced emission behaviors of TPP BF4 and TPP ClO4 were further demonstrated using water as a poor solvent as shown in Fig. S5 (ESI<sup>†</sup>), indicating that the aggregated or solid state guarantees the generation of transient phosphorescence for TPP BF<sub>4</sub> and TPP ClO<sub>4</sub>.

#### Mechanistic investigation on anion-regulated transient and persistent phosphorescence

Low-temperature experiments were performed with dilute solutions of TPP Cl, TPP BF4 and TPP ClO4 to explore the origins of their transient emissions at 420 nm. Fig. S6 (ESI<sup>+</sup>) shows that an apparent emission peak is gradually intensified with the decrease of the temperature from 300 K to 77 K for each solution, indicating that these emissions around 420 nm originate from dissolved ion pairs. The consistency in emission maxima and lifetimes (Fig. S7, ESI†) between the lowtemperature glassy state and the solid state for each of them suggests that separated monomers mainly contribute to the transient emissions at around 420 nm in the crystals. The emission enhancement trend with the decrease of the temperature excludes the possibility of the emission origin from thermally activated delayed fluorescence. It is generally known that the heavy atom effect due to heavy atoms like bromine and iodine apparently facilitates intersystem crossing processes, thus greatly boosting the triplet emission.<sup>19</sup> However, these three crystals do not contain heavy atoms. As a result, it is rational to deduce that intermolecular charge transfer during the excitation process appreciably promotes the intersystem crossing rate from the S<sub>1</sub> state to its neighbouring triplet state.<sup>9</sup> To verify this hypothesis, density functional theory (DFT) and time-dependent density functional theory (TDDFT) were employed to analyze their molecular orbitals and electron density change between ground states and excited states. All the HOMOs and LUMOs of TPP Cl, TPP BF4 and TPP ClO4 can be visualized in Fig. 3. It is surprisingly noted that all the HOMOs are mainly composed of atomic orbitals of the anions, while the p orbitals of



**Fig. 3** HOMOs and LUMOs of TPP Cl (a), TPP BF<sub>4</sub> (b) and TPP ClO<sub>4</sub> (c) monomers, and Jablonski diagrams of TPP Cl (d), TPP BF<sub>4</sub> (e) and TPP ClO<sub>4</sub> (f) monomers with labeled energy gaps from TDDFT calculations. The energy gaps between  $T_1$  and  $S_0$  for TPP Cl, TPP BF<sub>4</sub> and TPP ClO<sub>4</sub> determined experimentally were 2.500, 2.884 and 2.938 eV, respectively, according to their respective PL spectra.

aromatic carbon atoms in the TPP moiety dominantly contribute to the LUMOs of TPP Cl, TPP BF<sub>4</sub> and TPP ClO<sub>4</sub>. Such separated locations of the HOMOs and LUMOs are an indication of the significant charge transfer character for these ionic compounds. The electron density difference maps in Fig. S8 (ESI<sup>†</sup>) clearly demonstrate appreciable charge transfer trends from anions to the TPP moiety for all of them. It is reported that the occurrence of charge transfer during excitation is favoured to lower the energy gap between S<sub>1</sub> and its neighbouring triplet state, and thus results in the enhancement of the intersystem crossing rate and phosphorescence proportion.<sup>20</sup> Consequently, the energy differences between S<sub>1</sub> and its neighbouring triplet state ( $\Delta E_{ST}$ ) for TPP Cl, TPP BF<sub>4</sub> and TPP ClO<sub>4</sub> are calculated using TDDFT and labelled in their Jablonski diagrams in Fig. 3. According to the Fermi golden rule,<sup>21</sup> the intersystem crossing rate can be described as

$$k_{\rm ISC} = \frac{2\pi}{\hbar} \langle \psi^1 | H_{\rm SO} | \psi^3 \rangle^2 \times \text{FCWD}$$

where the former term in this equation is related to the spin-orbit coupling effect caused by heavy atoms, and the latter term FCWD is inversely proportional to the value of  $\Delta E_{ST}$ . The much smaller values calculated for TPP BF<sub>4</sub> (0.008 eV) and TPP ClO<sub>4</sub> (0.001) than that of TPP Cl (0.185 eV) provide direct proof that TPP BF<sub>4</sub> and TPP ClO<sub>4</sub> have much greater intersystem crossing rates ( $k_{IST}$ ) than that of TPP Cl, which indicates the highly bright room-temperature phosphorescence of TPP BF<sub>4</sub> and TPP ClO<sub>4</sub> crystals. Lowering the energy gap between S<sub>1</sub> and its neighboring triplet state through construction of donor-acceptor patterns in molecular structures can act as a general design strategy to realise heavyatom free organic phosphors with highly efficient room-temperature phosphorescence.

Differing from TPP  $BF_4$  crystals, TPP  $ClO_4$  crystals not only exhibit ultrabright transient phosphorescence under the irradiation but also exhibit highly efficient green afterglow after ceasing the excitation. Since it has been revealed that strong intermolecular electronic coupling with specific molecular arrangement in crystals is responsible for persistent emission



**Fig. 4** Ionic arrangements with labeled distances of TPP  $BF_4$  viewed along the *a*-axis, *b*-axis and *c*-axis (a–c), and ionic arrangements with labeled distances of TPP  $ClO_4$  viewed along the *a*-axis, *b*-axis and *c*-axis (d–f).

of pure organic materials,<sup>14</sup> we postulate that appreciable interionic electronic coupling occurs for TPP ClO<sub>4</sub>, whereas interionic interaction in TPP BF<sub>4</sub> is relatively weak. To validate this hypothesis, ionic arrangement in a single crystal is analyzed for TPP BF4 and TPP ClO4. It is readily concluded that the ionic packing diagrams of TPP BF4 and TPP ClO<sub>4</sub> are very similar from their crystallographic data listed in Table S3 (ESI<sup>†</sup>) because both the crystals belong to the same space group 14 and possess very similar lattice parameters. Fig. 4 shows ionic packing diagrams of TPP BF4 and TPP ClO4 along the a-axis, b-axis and c-axis, which clearly demonstrates that they have similar ionic packing patterns in the different directions. By viewing the ionic arrangements along the *c*-axis for TPP BF<sub>4</sub> and TPP ClO<sub>4</sub> as shown in Fig. 4c and f, it is noted that the  $BF_4^{-}$  or  $ClO_4^{-}$  anions are homogeneously filled in the cavities surrounded by TPP cations, and the distances between the central atoms of BF<sub>4</sub><sup>-</sup> and its two neighboring TPP cations for TPP BF<sub>4</sub> (6.28 and 8.01 Å) are almost identical to those for TPP  $ClO_4$  (6.31 and 8.03 Å), suggesting that the sizes of the cavities surrounded by TPP cations are almost the same for TPP BF4 and TPP ClO<sub>4</sub>. However, the thermochemical radius of ClO<sub>4</sub><sup>-</sup> (2.25 Å) is much larger than that of  $BF_4^-$  (2.05 Å) according to ref. 22, which leads to a greater volume of  $ClO_4^-$  by 33% than  $BF_4^-$ . Such a greater space occupation of  $ClO_4^-$  than  $BF_4^-$  in the identical cavity would cause a stronger interaction between ClO<sub>4</sub><sup>-</sup> and TPP cations in the crystal, and such a strong ionic interaction between ClO4- and TPP cations might greatly contribute to the generation of the afterglow of TPP ClO<sub>4</sub> crystals. As a result, it is rational to ascribe the ultrabright afterglow of TPP ClO<sub>4</sub> crystals to the combination of the enhancing intersystem crossing rate and the intensifying interionic interaction in the crystals by lowering the energy gap  $\Delta E_{\rm ST}$ and unique crystal arrangement. To further substantiate the ultralong green emission due to the aggregation behaviour of TPP ClO<sub>4</sub> crystals, the photophysical properties of three TPP ClO<sub>4</sub> crystals with different sizes are compared. Large crystals are several millimeters in length, but small crystals obtained by grinding the large crystals are not uniform with diameters greater than 25  $\pm$  10  $\mu$ m, while microcrystals obtained by fast precipitation have the smallest size around 1  $\pm$  0.5  $\mu m$  with uniform



Fig. 5 XRD patterns (a), PL spectra (b) and afterglows (c) of large crystals, small crystals and microcrystals of TPP  $ClO_4$ .

shape (Fig. S9, ESI<sup>+</sup>). The almost identical XRD patterns among these crystals in Fig. 5a indicate that their crystal structures are the same, but their PL emissions completely change as shown in Fig. 5b. In comparison with large crystals, the afterglow intensity at 470 nm of small crystals apparently decreases, and the afterglow of microcrystals completely disappears. The time-resolved PL decay curve of small crystals demonstrates that their afterglow lifetime is also largely shortened to 417.9 ms (Fig. S10, ESI<sup>+</sup>), and the afterglow emission almost completely disappears for microcrystals according to its lifetime change (Fig. S11, ESI<sup>+</sup>). Fig. 5c also illustrates both the emission duration and brightness sharply decrease in the order of large crystals, small crystals and microcrystals. To further acquire quantitative relation between crystal size and the relative intensity of the afterglow, additional three crystals with different average diameters were prepared and characterized using XRD and SEM (Fig. S12 and S13, ESI<sup>+</sup>). Their crystal packing arrangements are the same, but their average diameters fall in a large size range from 0.5 to 5000 µM. The PL spectra of these crystals in Fig. S14 (ESI<sup>†</sup>) show a clear decreasing trend for the afterglow emission with the decrease in the size of the crystals. A quantitative relation can be obtained between the relative intensity of the afterglow and the average size of the crystals (Fig. S15, ESI<sup>+</sup>), and a similar decreasing trend in the lifetime of the afterglow with the decrease in crystal size is also found (Fig. S16, ESI<sup>+</sup>). These observations evidently support that the afterglow of TPP ClO<sub>4</sub> crystals is a result of their aggregation behaviour and their ultrabright RTP is not size-dependent due to its origin from a couple of ionic pairs. This is the first time that direct evidence has been provided to show that the ultralong afterglow of organic crystals is size-dependent and originates from aggregates in the crystals, and it offers a convincing design rule to achieving efficient ultralong afterglow of organic materials.

# Phosphorescence turn-on detection of perchlorate ions and *in vivo* imaging

TPP Cl is soluble in water, but TPP  $ClO_4$  is highly insoluble in aqueous solution and exists as microcrystals when it is

precipitated from water. The high quantum yield of TPP ClO<sub>4</sub> (0.56) enables TPP Cl to act as a phosphorescence turn-on molecular probe for perchlorate ions in aqueous solution. Fig. 6a shows the gradual increase in phosphorescence intensity when different amounts of ClO<sub>4</sub><sup>-</sup> are added into a TTP Cl solution (100.0 µM), where an increasing amount of TPP ClO<sub>4</sub> microcrystals is formed with continuous introduction of perchlorate ions. A good linear relationship between the PL intensity and  $\text{ClO}_4^-$  concentration in the range of 3.3–60.0  $\mu\text{M}$  is found (Fig. S17, ESI<sup>+</sup>), and the detection limit from three time standard deviations is estimated to be 0.08 µM, which is comparable to that based on an ionic iridium complex (0.05 ppm).<sup>23</sup> No response is observed when the other 14 common anions are introduced into the same TPP Cl solution because these anions do not create luminescent precipitates under such conditions (Fig. 6b). The long lifetime of TPP ClO<sub>4</sub> microcrystals (3.5 µs) allows us to establish the first time-gated luminescent detection method for perchlorate ions. Human serum as a typical example with strong blue autofluorescence is used to evaluate the time-gated luminescent assay for ClO<sub>4</sub><sup>-</sup>. PL spectra of the serum sample are recorded upon progressively increasing the concentration of  $ClO_4^-$  after a delay time of 5.0 ms is applied because under such conditions the interference from autofluorescence is almost completely eliminated. The PL intensity gradually increases with ClO<sub>4</sub><sup>-</sup> concentration, and a broad linear scope in the range of 0.1-120.0 µM is established (Fig. S18, ESI<sup>+</sup>). Because the bright blue phosphorescence originates from the solid form of TPP ClO<sub>4</sub>, a facile test strip containing a certain amount of TPP Cl



**Fig. 6** (a) PL spectra of TPP Cl solution (100.0  $\mu$ M) with the addition of different amounts of perchlorate ions from 0.0 to 100.0  $\mu$ M. (b) Selectivity test of TPP Cl (100.0  $\mu$ M) towards perchlorate ions (50.0  $\mu$ M). Letters a–o represent NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, S<sup>2-</sup>, ClO<sub>3</sub><sup>-</sup>, IO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and ClO<sub>4</sub><sup>-</sup>, respectively. (c) Laser scanning confocal microscopy image of a seedling root of *Arabidopsis thaliana* with TPP Cl (100.0  $\mu$ M). (d) Laser scanning confocal microscopy image of a seedling root of *Arabidopsis thaliana* with TPP Cl (100.0  $\mu$ M) and ClO<sub>4</sub><sup>-</sup> (100.0  $\mu$ M). Scale bar: 50  $\mu$ m; excitation wavelength: 355 nm; collection wavelength: 410–450 nm.

can be fabricated for the determination of  $\text{ClO}_4^-$ . The PL intensity of the test strip progressively increases upon continuously adding  $\text{ClO}_4^-$  solution, and a very low detection limit (5.0 ng) can be achieved in terms of its calibration curve between the PL intensity and the  $\text{ClO}_4^-$  amount in Fig. S19 (ESI†). Even by the naked eye a very small amount of  $\text{ClO}_4^-$  as low as 25.0 ng can be readily identified from its blue phosphorescence on the test strip, and the test strip also shows excellent selectivity for  $\text{ClO}_4^-$ .

The high brightness and outstanding specificity of the established assay for ClO<sub>4</sub><sup>-</sup> encourage us to validate it in more complex biological matrices. Perchlorate ions as a hazardous pollutant frequently can accumulate in plants, and cause slow growth and death of the plants.<sup>24</sup> We adopt a seedling root of Arabidopsis thaliana as a model to evaluate the feasibility of the established method for  $ClO_4^-$  because its seedling root is able to allow blue light to penetrate through it and absorb a small amount of ClO<sub>4</sub><sup>-</sup>. Fig. 6c shows a low-intensity blue background from the autofluorescence of Arabidopsis thaliana after the seedlings are incubated in a TPP Cl solution (100.0 µM) for 30 min, but bright blue images can be recorded after introducing a certain amount of ClO<sub>4</sub><sup>-</sup>. A gradual enhancement of the blue emission from the root tip to the body in Fig. 6d dictates that ClO<sub>4</sub><sup>-</sup> penetrates into the root of Arabidopsis thaliana through root tips. Differing from the homogeneous emission of traditional dyes, the signals from TPP ClO<sub>4</sub> microcrystals scattered inside the root emerge in dot-like shape without any diffusion. A progressive absorption of ClO<sub>4</sub><sup>-</sup> into the root of Arabidopsis thaliana is clearly reflected through the gradual extension of the blue signal from the root tip to the body (Fig. S20, ESI<sup>†</sup>). The photostability of TPP ClO<sub>4</sub> microcrystals is also assessed by continuous irradiation with UV light, and Fig. S21 (ESI<sup>†</sup>) illustrates that the blue phosphorescence intensity shows no appreciable decrease after 15 min, indicating the excellent resistance of precipitating TPP ClO<sub>4</sub> to photobleaching.

# Time-dimensional anti-counterfeiting of school badges and banknotes

The short-emitting blue phosphorescence of microcrystals and the ultralong green afterglow of small and large crystals of TPP ClO<sub>4</sub> provide an opportunity to demonstrate their specific function in anti-counterfeiting. As shown in Fig. 7a, the outer circle of our school badge is made of TPP ClO<sub>4</sub> microcrystals, while the inner pattern is composed of small crystals and large crystals. A bright blue school badge appears under a UV lamp, but a sharp contrast in emission can be achieved after turning off the lamp. The outer circle is quickly darkened in one second, whereas the inner pattern still shines in green color for more than 4 s. Another important application of emissive anti-counterfeiting is on banknotes, which generally contain short-lived fluorescent dyes in specific areas. For example, the denomination 100 and the serial number for a 100 banknote are separately marked with bright yellow and green fluorescence as part of anti-fake function. When a similar pattern made of small TPP ClO<sub>4</sub> crystals to the yellow-emitting area on the banknote is utilized, an additional time-dimensional



**Fig. 7** (a) A demonstration of anti-counterfeiting function in a school badge of Zhejiang Normal University. (b) A demonstration of time-dimensional anti-counterfeiting of a 100 banknote. The images are taken under a 365 nm UV lamp and after ceasing the excitation.

anti-counterfeiting function is introduced besides the addition of two different colours. In this case, anti-counterfeiting of banknotes can be greatly enhanced with several dimensions. These demonstrations offer attractive and huge application prospects in anti-counterfeiting, and will greatly promote the fast development of organic materials with ultrabright roomtemperature phosphorescence and ultralong afterglow.

# Conclusions

In summary, the transient and persistent room-temperature phosphorescence of tetraphenylphosphonium-based organic ionic crystals can be regulated by anions, and appropriate anions greatly promote the occurrence of triplet emission by lowering the energy gap between the first singlet state and its neighboring triplet state of the formed ionic crystals. Achievement of extraordinarily efficient transient phosphorescence by rational construction of such a donor-acceptor pattern in the crystals contributes to general design principles. The afterglow brightness of tetraphenylphosphonium perchlorate largely relies on the size of the crystals, and such a size-dependent behavior provides direct and solid proof that the afterglow is generated from aggregates with strong interionic interactions in the crystals. In combination with structural design boosting the intersystem crossing processes, large aggregates consisting of ordered units with significant intermolecular electronic coupling greatly favor the occurrence of organic afterglow. This design rule will be enormously valuable to design and accomplishment of diverse organic materials with highly bright organic afterglow in the future. The establishment of a highly specific detection method for perchlorate ions and the demonstration of time-dimensional anti-counterfeiting based on the unique phosphorescence properties of TPP ClO<sub>4</sub> crystals illustrate their bright prospects and potential use in various fields. Organic phosphonium crystals are expected to exhibit bright room-temperature phosphorescence and ultralong afterglow by proper molecular design and anion regulation, and these organic crystals will show huge potential in diverse applications.

## Conflicts of interest

There are no conflicts to declare.

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