Electronic Supplementary Information *for*

Anion-Regulating Transient and Persistent Phosphorescence and Size-Dependent Ultralong Afterglow of Organic Ionic Crystals

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1. Experimental Details.

Materials and Reagents. Triple-distilled water was utilized throughout the whole experimental process. Tetraphenylphosphonium chloride (TPP Cl) was purchased from Sigma-Aldrich Company (Shanghai, China). All sodium salts including Sodium perchlorate (NaClO₄) and sodium tetrafluoroborate (NaBF₄) were bought from J&K Scientific Company (Shanghai, China). HEPES solution (10 mM, pH 7.4) was used as the buffer solution. All reagents were of analytical grade and TPP Cl was recrystallized for further use.

Characterization of Solid-State Photoluminescence of All Samples. Steady PL spectra of all samples were performed on an Edinburgh Instruments model FLS980 fluorescence spectrophotometer equipped with a xenon arc lamp using a front face sample holder. Time-resolved measurement for fluorescence was conducted with EPL-series lasers, and long-lived measurement for phosphorescence was carried out with a μ F2 microsecond flashlamp. Time-delayed PL spectra were recorded using a μ F2 microsecond flashlamp and a time-gated module. All the emission efficiencies in this work were determined using an absolute method with a Teflon integrating sphere.

Characterization of Tetraphenylphosphonium Chloride (TPP Cl). TPP Cl was purchased from Sigma-Aldrich Company (Shanghai, China), and purified through multiple recrystallization. TPP Cl was further characterized using ¹H NMR, ¹³C NMR, ³¹P NMR, high-resolution mass spectrometry and high-performance liquid chromatography, respectively. ¹H NMR (600 MHz, CD₃CN) δ (ppm) 7.67-7.70 (m, 8H), 7.73-7.76 (m, 8H), 7.91-7.93 (m, 4H). ¹³C NMR (150 MHz, CD₃CN) δ (ppm) 118.6, 119.2, 131.3, 135.7, 136.4. ³¹P NMR (243 MHz, CD₃CN) δ (ppm) 22.87. MS (ESI⁺, m/z): 339.1295 [C₂₄H₂₀P]⁺.

Synthesis and Characterization of Tetraphenylphosphonium Tetrafluoroborate (TPP BF₄). A typical procedure for synthesis of TPP BF₄ was as follows. Tetraphenylphosphonium chloride (1.13 g, 3.0 mmol) and sodium tetrafluoroborate (0.33

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g, 3.0 mmol) were added into a fixed amount of water (50 mL), and the resulting mixture was fully stirred for 1 h. A large amount of white TPP BF₄ precipitate was generated during the stirring, and was further filtered to acquire the final product TPP BF₄. The resulting precipitates (TTP BF₄) were dried and further recrystallized in acetonitrile. TPP BF₄ was characterized using ¹H NMR, ¹³C NMR, ³¹P NMR, ¹⁹F NMR, high-resolution mass spectrometry and high-performance liquid chromatography, respectively. ¹H NMR (600 MHz, CD₃CN) δ (ppm) 7.66-7.70 (m, 8H), 7.73-7.76 (m, 8H), 7.90-7.93 (m, 4H). ¹³C NMR (150 MHz, CD₃CN) δ (ppm) 118.7, 119.3, 131.4, 135.8, 136.4. ³¹P NMR (243 MHz, CD₃CN) δ (ppm) 22.91. ¹⁹F NMR (565 MHz, CD₃CN) δ (ppm) -151.73. MS (ESI⁺, m/z): 339.1291 [C₂₄H₂₀P]⁺.

Synthesis of Tetraphenylphosphonium Perchlorate (TPP CIO₄). A typical procedure for synthesis of TPP CIO₄ was as follows. Tetraphenylphosphonium chloride (1.13 g, 3.0 mmol) and sodium perchlorate monohydrate (0.42 g, 3.0 mmol) were added into a fixed amount of water (50 mL), and the resulting mixture was fully stirred for 1 h. A great deal of white TPP CIO₄ precipitate was generated during the stirring, and was further filtered to get the final product TPP CIO₄ in the end. The resulting precipitates (TPP CIO₄) were dried and further recrystallized in acetonitrile. TPP CIO₄ was characterized using ¹H NMR, ¹³C NMR, ³¹P NMR, high-resolution mass spectrometry and high-performance liquid chromatography, respectively. ¹H NMR (600 MHz, CD₃CN) δ (ppm) 118.7, 119.3, 131.4, 135.7, 136.4. ³¹P NMR (243 MHz, CD₃CN) δ (ppm) 22.89. MS (ESI⁺, m/z): 339.1296 [C₂₄H₂₀P]⁺.

Structure Determination and Preparation of Single Crystals of TPP BF₄ and TPP ClO₄. The single crystals of TPP BF₄ and TPP ClO₄ were separately grown using their corresponding saturated solutions in acetonitrile by slow volatilization of the solvent. Their respective single crystals with suitable size were selected for single-crystal XRD determination. The intensity data were collected on a Bruker APEX II (1 and 2) with

graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed using the multiscan program. The structures were analyzed by direct methods and refined by full-matrix least squares on F² with the SHELX-97 program. All atoms except H were refined anisotropically. The crystal structures for TPP BF₄ and TPP ClO₄ have been deposited in the Cambridge Crystallographic Data Center (CCDC), and have been assigned as CCDC 1880252 and 1880253 respectively.

Preparation of Large Crystals, Small Crystals and Microcrystals of TPP ClO₄. Large crystals of TPP ClO₄ in millimeter magnitude were prepared via natural volatilization of a saturate TPP ClO₄ acetonitrile solution at room temperature. The small crystals were acquired by grinding large crystals in a quartz mortar. Microcrystals were obtained from a precipitating reaction between tetraphenylphosphonium chloride and sodium perchlorate in water. X-ray powder diffraction patterns of the three crystals of TPP ClO₄ were recorded on a Philips PW3040/60 model X-ray powder diffractometer.

Preparation of Large Crystal-1, Large Crystal-2, Small Crystal-1, Small Crystal-2, Microcrystal-1 and Microcrystal-2 of TPP ClO₄. Large crystal-1 and large crystal-2 of TPP ClO₄ in millimeter magnitude were prepared via natural growth at different time with a saturate TPP ClO₄ acetonitrile solution. Small crystal-1 was prepared by adding a TPP ClO₄ acetonitrile solution into an ethyl acetate solution, and small crystal-2 was acquired by grinding large crystals in a quartz mortar. Microcrystal-1 and microcrystal-2 were obtained from a precipitating reaction by mixing an acetonitrile solution of TPP ClO₄ with different concentrations and excess water.

Quantitative Detection of Perchlorate ion Based on Tetraphenylphosphonium Chloride (TPP Cl). A TPP Cl solution with a fixed concentration (0.1 M) in HEPES buffer (pH 7.4) was first prepared, and then different amounts of perchlorate ions in the range of $0.0 - 100.0 \mu$ M were separately added into the preceding TPP Cl solution. The PL spectra of the resulting mixture were recorded at the excitation of 330 nm using a xenon arc lamp. Selectivity test of the assay to perchlorate ion was conducted as follows. A certain amount of each chosen anion (100.0 μ M) such as NO₃⁻, PO₄³⁻, CO₃²⁻, CH₃CO₂⁻, SO₄²⁻, SO₃²⁻, S₂O₃²⁻, S²⁻, ClO₃⁻, IO₃⁻, F⁻, Cl⁻, Br⁻ and I⁻ was separately added into a TPP Cl solution (0.1 M) in HEPES buffer, and then the resulting solution was monitored using fluorescence spectrometer at 430 nm emission. For the time-gated detection of perchlorate ion, the protocol is same to the normal detection of perchlorate ion with the replacement of a xenon arc lamp with a µF2 microsecond flashlamp, and a delay time of 10.0 µs was used to acquire the PL spectra. A fixed amount of human serum (30.0 µL) in 3.0 mL of TPP Cl buffer solution was used as a complex matrix with a significant autofluorescence. All the detections were repeated at least three times.

Test Strips for Perchlorate ion Detection Based on Solid-Substrate Room-Temperature Phosphorescence. Fifty strips made from filter papers were first immersed in a concentrated TPP Cl solution (0.2 M) for 1 min, and then dried at room temperature to acquire test strips. A series of varying amounts of perchlorate ions in the range of 0.0 - $10.0 \mu g$ were separately dropped on the test strips, and the PL spectra of the resulting test strips were recorded at 370 nm excitation light and photographed under a UV lamp after they were dried. The selectivity test was run according to the preceding procedure by adding different anions including NO₃⁻, PO₄³⁻, CO₃²⁻, CH₃CO₂⁻, SO₄²⁻, SO₃²⁻, S₂O₃²⁻, S²⁻, ClO₄⁻, IO₃⁻, F⁻, Cl⁻, Br⁻, I⁻ and ClO₄⁻. The amount for each of them added on the test strip is 10.0 µg.

Laser Scanning Confocal Microscopy Imaging of Perchlorate Ion in Seedling Root of Live Arabidopsis Thaliana. Wild-type (Col-0) seeds were surface sterilized and imbibed for 3 days at 4 °C in dark and then sown onto $0.5 \times$ Murashige & Skoog (MS) 1.5% (w/v) agar plates. Seedlings were vertically grown on plates in a climate-controlled growth room (22/20 °C day/night temperature, 16/8-h photoperiod, and 80 µE s⁻¹ m⁻² light intensity). Five-day-old seedlings with healthy roots were used in this study unless otherwise specified. Phosphorescence imaging experiment was performed on a Leica TCS SP5 model confocal laser scanning microscope (Germany) with an excitation at 355 nm and a variable bandpass emission filter (410 – 450 nm). Five-day-old seedlings with healthy roots were divided into six groups. The first group acts as the blank. The second group was incubated with a 500.0 μ M TPP Cl solution for 15 min, and then washed three times with triple-distilled water. The third to sixth groups were first treated with a TPP Cl solution (500.0 μ M) for 15 min, and then incubated with a NaClO₄ solution (50.0 μ M) after these seedlings were washed with triple-distilled water, respectively. All six groups of seedlings were imaged using the confocal laser scanning microscope at the emission range of 410 – 450 nm.

Anti-Counterfeiting Applications on School Badges and Banknotes. The school badge of Zhejiang Normal University was made of large crystals, small crystals and microcrystals of TPP ClO₄. The outer circle was composed of TPP ClO₄ microcrystals, peak-like pattern was made up of small crystals, and the capitalized characters in the center consist of large crystals of TPP ClO₄. The school badge was photographed under the 365 nm UV light and after ceasing the UV light. A pattern containing the number 100 was pasted on a 100 banknote using small crystals of TPP ClO₄, and this pattern was photographed under the 365 nm UV light and after ceasing the UV light.

2. Computational Methods.

All the computations were performed using Gaussian 09 package.¹ To simulate actual structures in crystals to the greatest extent, the geometries of all compounds (TPP Cl, TPP BF₄ and TPP ClO₄) were first extracted from their corresponding crystal structures, and all the positions of hydrogen atoms were further optimized with B3LYP functional using density functional theory by fixing the positions of other atoms at 6-31+G(d,p) level.² The calculations of NBO analysis and electron density difference for all compounds were run at wB97XD/6-31+G(d,p) level, and their visualization was performed with Gview program.³ Excited state calculations were run at wB97XD/6-

31G(d) level for all the model compounds with time-dependent density functional theory (TD-DFT).⁴



3. Supplementary Figures

Figure S1. Purity tests of TPP Cl (a), TPP BF_4 (b) and TPP ClO_4 (c) crystals by high-performance liquid chromatography.



Figure S2. Crystal structures of single crystals of TPP BF₄ (CCDC 1880252) (a) and TPP ClO₄ (CCDC 1880253) (b) determined by single-crystal X-ray diffraction (Unit Å).



Figure S3. PL spectra (a), time-resolved decay curve (b) and ultralong afterglow (c) of TPP Cl crystals.



Figure S4. (a) Time-resolved PL decay curve of TPP BF_4 at 430 nm and (b) Time-resolved PL decay curve of TPP BF_4 at 490 nm.



Figure S5. PL spectra of dilute solutions of TPP BF₄ (a) and TPP ClO₄ (b) (10.0 μ M) with different water/acetonitrile ratios from 0% to 90%.



Figure S6. Temperature-dependent PL spectra of dilute solutions of TPP Cl (a), TPP BF₄ (b) and TPP ClO₄ (c) (10.0 μ M in acetonitrile) at different temperatures 77 K to 300 K.



Figure S7. Time-resolved PL decay curves of dilute solutions of TPP Cl (a), TPP BF₄ (b) and TPP ClO₄ (c) (10.0 μ M in acetonitrile) at 77 K.



Figure S8. Electron density difference maps of TPP Cl (a), TPP BF_4 (b) and TPP ClO_4 (c). Electron is transferred from blue area to cyan area.



Figure S9. SEM images of small crystals (a) and microcrystals (b) of TPP ClO₄.



Figure S10. Time-resolved PL decay curve of small crystals of TPP ClO₄.



Figure S11. Time-resolved PL decay curve of mcirocrystals of TPP ClO₄.



Figure S12. SEM images of TPP ClO_4 crystals with different average diameters. The average diameters of microcrystal-1 (d), microcrystal-2 (c), small crystal-1 (b), small crystal-2 (a), large crystal-1 and large crystal-2 are estimated to be 0.5, 2.5, 25, 100, 500 and 5000 µm, respectively.



Figure S13. XRD diagrams of TPP ClO₄ crystals with different average diameters.



Figure S14. PL spectra of TPP ClO₄ crystals with average diameters.



Figure S15. Quantitative relation between relative intensity of the afterglow and crystal size for TPP ClO₄.



Figure S16. Quantitative relation between lifetime of the afterglow and crystal size for TPP ClO_4 .



Figure S17. Calibration curve between PL intensity and the concentration of ClO_4^- in the range of $3.3 - 60.0 \mu$ M in aqueous solution.



Figure S18. (a) PL spectra of TPP Cl in serum versus the amount of ClO_4^- in the range of $0.0 - 120.0 \ \mu\text{M}$ with a delay time of 5.0 ms. (b) Calibration curve between PL intensity and the concentration of ClO_4^- in the range of $0.1 - 120.0 \ \mu\text{M}$ in serum.



Figure S19. (a) PL spectra of TPP Cl on a test strip versus the amount of ClO_4^- in the range of $0.0 - 15.0 \ \mu$ g. (b) Calibration curve between PL intensity and ClO_4^- amount in the range of $0.025 - 8.0 \ \mu$ g. (c) Phosphorescence images of test strips with the addition of different amounts of ClO_4^- . (d) Selectivity test of the test strip. The number 1 - 14 represents NO_3^- , PO_4^{3-} , CO_3^{2-} , $CH_3CO_2^-$, SO_4^{2-} , SO_3^{2-} , $S^2O_3^{2-}$, S^2- , ClO_3^- , IO_3^- , F^- , Cl^- , Br⁻, I⁻ and ClO_4^- , respectively.



Figure S20. Laser scanning confocal microscopy images of seedling root of *arabidopsis thaliana* previously incubated with a TPP Cl solution (100.0 μ M) in the presence of a ClO₄⁻ solution (100.0 μ M) for different times: (a) 5 min, (b) 10 min, (c) 15 min and (d) 20 min.



Figure S21. Laser scanning confocal microscopy images of seedling root of *arabidopsis thaliana* containing TPP CIO_4 at different periods of irradiation at 354 nm: (a) 0 min, (b) 5 min, (c) 10 min and (d) 15 min.

4. Supplementary Tables

Table S1. Photoluminescence properties of tetraphenylphosphonium chloride (TPP Cl), tetraphenylphosphonium tetrafluoroborate (TPP BF_4), and tetraphenylphosphonium perchlorate (TPP ClO_4) in crystal form at 298 K.

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	$\lambda_{ex} (nm)^{[a]}$	$\lambda_{em} (nm)^{[b]}$	T ^[c]	$\Phi^{[d]}$
	308	400	0.9 ns	< 0.01
TPP Cl	308	500	7.3 ms (59%) 253.2 ms (41%)	0.02
	330	430	4.5 µs	0.48
TPP BF ₄	330	490	6.1 ms (86%) 272.6 ms (14%)	< 0.01
	341	420	2.8 µs	
TPP ClO ₄	341	475	15.5 ms (59%) 952.6 ms (41%)	0.56 ^e

^[a] Excitation maximum. ^[b] Emission maximum. ^[c] Lifetimes. ^[d] Quantum yield. ^[e] Total Quantum Yield.

Table S2. Excitation energies of first 20 states for TPP Cl, TPP BF_4 and TPP ClO_4 calculated with TDDFT.

State No	TPP Cl	TPP BF ₄	TPP CIO ₄
1	2.6408 eV (T ₁)	3.7855 eV (T ₁)	3.6216 eV (T ₁)
2	2.8260 eV (S ₁)	3.7947 eV (T ₂)	3.6223 eV (S ₁)
3	2.9000 eV (T ₂)	3.8004 eV (T ₃)	3.6304 eV (T ₂)
4	2.9769 eV (S ₂)	3.8121 eV (T ₄)	3.6392 eV (S ₂)
5	2.9812 eV (T ₃)	4.3740 eV (T ₅)	3.7592 eV (T ₃)
6	3.0833 eV (S ₃)	4.4228 eV (T ₆)	3.7674 eV (T ₄)
7	3.1127 eV (T ₄)	4.5674 eV (T ₇)	3.7717 eV (T ₅)
8	3.1297 eV (T ₅)	4.5950 eV (T ₈)	3.7732 eV (S ₃)
9	3.1344 eV (S ₄)	4.7987 eV (T ₉)	3.7771 eV (T ₆)
10	3.2017 eV (S ₅)	4.8065 eV (S ₁)	3.7880 eV (T ₇)
11	3.2288 eV (T ₆)	4.8072 eV (T ₁₀)	3.9615 eV (T ₈)
12	3.2826 eV (S ₆)	4.8206 eV (S ₂)	3.9639 eV (S ₄)
13	3.3089 eV (T ₇)	4.8423 eV (T ₁₁)	3.9718 eV (T ₉)
14	3.3329 eV (T ₈)	4.8495 eV (T ₁₂)	3.9828 eV (S ₅)
15	3.3389 eV (S ₇)	4.8554 eV (S ₃)	4.0896 eV (T ₁₀)
16	3.3677 eV (S ₈)	4.8623 eV (T ₁₃)	4.0917 eV (S ₆)
17	3.3873 eV (T ₉)	4.9041 eV (S ₄)	4.1058 eV (T ₁₁)
18	3.3964 eV (S ₉)	4.9048 eV (T ₁₄)	4.1064 eV (S ₇)
19	3.4654 eV (T ₁₀)	5.1624 eV (S ₅)	4.1244 eV (T ₁₂)
20	3.7955 eV (S ₁₀)	5.1625 eV (T ₁₅)	4.1253 eV (S ₈)

source	TPP BF ₄	TPP ClO ₄
Chemical formula	$C_{24}H_{20}BF_4P$	$C_{24}H_{20}ClO_4P$
Formula weight	426.1940	438.8400
temperature	293	293
wavelength (Å)	0.71073	0.71073
crystal system	tetragonal	tetragonal
space group	I4	I4
a	12.06730	12.12273
b	12.06730	12.12273
c	7.01830	7.03110
α	90.00	90.00
β	90.00	90.00
γ	90.00	90.00
volume	1022.0	1033.29

Table S3. Crystallographic data for TPP BF₄ and TPP ClO₄

5. Spectra of Compounds







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¹³C NMR spectrum of TPP BF₄ in CD₃CN







¹³C NMR spectrum of TPP ClO₄ in CD₃CN



13P N	MR	spectrum	of TPP	ClO ₄	in	CD ₃ C	N
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6.	Car	tesian	Coor	dinates

TPP Cl			
Cl	5.52966800	9.53736400	2.01040000
Р	7.84940200	5.35760600	1.57610300
С	6.91330000	4.30070000	0.49010100
С	6.11510100	3.30369900	1.02460000
С	5.51430000	2.37700000	0.20230000
С	5.68700000	2.44820000	-1.16160000
С	6.45680000	3.44140000	-1.70700000
С	7.07320000	4.37000000	-0.90049900
С	9.42940100	4.57120200	1.89180100
С	10.22030000	4.93880000	2.97420000
С	11.44930000	4.34020000	3.15640000
С	11.90680000	3.40480000	2.27960000
С	11.14250000	3.02850000	1.20390000
С	9.89880100	3.60400200	1.00629900
С	8.10747700	6.94717200	0.80460900
С	7.08422200	7.52653100	0.04437700

-22.89

С	7.21000400	8.81222000	-0.42717800
С	8.34540100	9.53499200	-0.15869700
С	9.38430400	8.96719800	0.55229000
С	9.26860000	7.68050300	1.03340200
С	6.92249000	5.60568500	3.08886600
С	5.79721100	6.42760700	3.04325700
С	5.02195000	6.60756200	4.16507500
С	5.37008100	5.99057900	5.33750300
С	6.47609800	5.19379600	5.39970000
С	7.25048900	4.98208200	4.27569300
Н	5.96272100	3.24541800	2.09844800
Н	4.89291100	1.59877300	0.63555400
Η	5.20576400	1.71804500	-1.80655600
Н	6.58225500	3.50587800	-2.78428200
Н	7.68446400	5.15125200	-1.34073300
Η	9.88470200	5.69712900	3.67380600
Η	12.05736400	4.63423900	4.00756600
Н	12.88074100	2.94812100	2.43508800
Н	11.50237000	2.27843800	0.50594000
Η	9.29717300	3.29159800	0.16038300
Н	6.15825900	6.99263200	-0.13945000
Н	6.38161500	9.26451700	-0.95815500
Н	8.42115200	10.56386900	-0.49715400
Н	10.28716000	9.53544000	0.75531800
Н	10.09010000	7.25297200	1.59969300
Н	5.55015900	7.02700800	2.17030300
Н	4.18215400	7.29178500	4.10613700
Н	4.77032400	6.14929100	6.23057600
Н	6.75346000	4.70976300	6.33231400
Н	8.10394400	4.31601700	4.34599900
TPP BF ₄			
Р	0.00000100	12.06699600	7.01800000
С	-1.20299900	11.26150000	8.07560000
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