Supplementary Information

for the letter entitled

Intense Fluorescence of 1-Aryl-2,3,4,5-tetraphenylphosphole Oxides in the Crystalline State

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1. Experimental Detail

General. Melting points (mp) were determined with a Stanford Research Systems OptiMelt MPA100 instrument. ¹H NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz) in CDCl₃ and chemical shifts are reported in δ ppm using CHCl₃ (7.26 ppm) as an internal standard. ¹⁹F and ³¹P NMR spectra were recorded with a JEOL AL-400 spectrometer (376 MHz for ¹⁹F and 162 MHz for ³¹P) using CFCl₃ (0.0 ppm for ¹⁹F) and H₃PO₄ (0.0 ppm for ³¹P) as an external standard, respectively. Mass spectra were measured with a JEOL JMS 700. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of Silica Gel 60 F_{254} (Merck). Column chromatography was performed using silica gel PSQ 100B (Fuji Silysia Chemical). Recycle preparative high performance liquid chromatography (HPLC) was performed using LC-918 (Japan Analytical Industry) equipped with a reversed phase column (Wakosil-II 5C18 HG Prep, Wako). Recycle preparative gel permeation chromatography (GPC) was performed using LC-918 equipped with polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with CHCl₃ as an eluent. Diphenylacetylene and lithium (granular) was purchased from Kanto Chemicals and Chemetal GmbH, respectively, and used as received. Anhydrous Et₂O and THF were purchased from Kanto Chemicals. Compound 6^1 and 7^2 were synthesized according to the literature methods. All reactions were performed under an argon atmosphere, unless stated otherwise.

1,2,3,4,5-Pentaphenyl-1H-phosphole-1-oxide (1). 1 was prepared by modification of the method reported in the literature.² Thus, to the suspension of lithium (granular, 37 mg, 20 mmol) in dry Et₂O (20 mL) was added diphenylacetylene (0.95 g, 5.3 mmol) at room temperature. After stirring for 24 h, the reaction mixture was cooled to 0 °C. After complete freeze of this mixture, PhPCl₂ (3.5 mL, 40 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 19 h at the same temperature. After removal of Et₂O under reduced pressure, dry THF (27 mL) was added and the mixture was cooled to 0 °C. A H₂O₂ aqueous solution (30%, 4.5 mL) was added at 0 °C and the resulting mixture was allowed to warm to be ambient temperature again. After stirring for 3 h, a Na₂SO₃ aqueous solution (10%, 1.2 mL) was added at 0 °C. After removal of THF under reduced pressure, a Na₂SO₃ aqueous solution (10%, 16 mL) was added and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water and brine, and dried over Na₂SO₄. After concentration of the organic layer, the mixture was purified by column chromatography (PSQ100B, 15/1 CHCl₃/AcOEt, $R_{\rm f}$ = 0.20) to afford 713 mg (1.48 mmol) of 1 in 56% yield as yellow solids: mp 282–283 °C. 1 H NMR (CDCl₃, 400 MHz): 8 6.92–6.95 (m, 4H), 7.04–7.19 (m, 16H), 7.43–7.50 (m, 3H), 7.93–7.98 (m, 2H). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ 44.79. HRMS Calcd for C₃₄H₂₅OP: 480.1643. Found: 480.1634.

1-Mesityl-2,3,4,5-tetraphenyl-1H-phosphole-1-oxide (2). To a suspension of lithium (granular, 139 mg, 20 mmol) in dry Et₂O (20 mL) was added diphenylacetylene (3.74 g, 21 mmol) at room temperature. After stirring for 23 h, the reaction mixture was cooled to -196 °C by using liquid nitrogen. After complete freeze of this mixture, PCl₃ (3.5 mL, 40 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 24 h at the same temperature. After removal of Et₂O and remaining PCl₃ under reduced pressure, dry THF (10 mL) was added and the mixture was cooled to 0 °C. Mesityllithium prepared in situ from bromomesitylene (1.99 g, 10 mmol) and t-BuLi (1.57 M solution in pentane, 12.8 mL, 20 mmol) in dry THF (10 mL) at -78 °C was added dropwise at 0 °C and the reaction temperature was allowed to warm to be ambient temperature. After stirring for 24 h, H₂O₂ aq. (30%, 4.5 mL) was added at 0 °C and the resulting mixture was allowed to warm to be ambient temperature again. After stirring for 18 h, the reaction was quenched by addition of Na₂SO₃ aq. (10%, 50 mL) at 0 °C. After evaporation of THF under reduced pressure, Na₂SO₃ aq. (10%, 150 mL) was added and the organic layer separated. The aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water and brine, and dried over Na₂SO₄. After concentration of the organic layer, residual crude product was purified by column chromatography (PSQ100B, 20/1 CH₂Cl₂/AcOEt as eluent, $R_{\rm f}$ = 0.27) to afford 1.57 g of 2 (3.0 mmol, 30% yield) as yellowish green solids: mp 192–193 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.26 (s, 3H), 2.70–2.82 (br, 6H), 6.88–6.90 (m, 6H), 7.04–7.17 (m, 16H). ${}^{31}P{}^{1}H$ NMR (CDCl₃, 162 MHz) δ 50.60. HRMS Calcd for C₃₇H₃₁OP: 522.2113. Found: 522.2115.

2,3,4,5-Tetraphenyl-1-(2',4',6'-triisopropylphenyl)-1*H*-phosphole-1-oxide (3). This compound was prepared from lithium (granular, 137 mg, 20 mmol), diphenylacetylene (3.74 g, 21 mmol), PCl₃ (3.5 mL, 40 mmol) and *in-situ* generated 2,4,6-triisopropylphenyllithium from 1-bromo-2,4,6-triisopropylbenzene 2.8 g, 10 mmol) and *t*-BuLi (1.57 M solution in pentane, 13 mL, 20 mmol) in dry THF (10 mL) in the similar manner as described for **2**. After separation by column chromatography (30/1 CHCl₃/AcOEt, $R_f = 0.17$), thorough purification using preparative GPC and reversed-phase HPLC afforded 165 mg (0.27 mmol) of **3** in 3% yield as yellowish green solids: mp 210–211 °C. ¹H NMR (CDCl₃, 400 MHz) δ 1.19 (d, *J* = 6.8 Hz, 12H), 2.86 (d, *J* = 6.8 Hz, 1H), 4.15 (br, 1H), 5.14 (br, 1H), 6.91 (dd, *J* = 8.0 Hz, 1.6 Hz, 4H), 7.01–7.20 (m, 18H). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 51.47. HRMS Calcd for C₃₇H₃₁OP: 606.3052. Found: 606.3046.

1-(4'-Methoxyphenyl)-2,3,4,5-tetraphenyl-1*H*-phosphole-1-oxide (4). This compound was prepared from lithium (granular, 69 mg, 10 mmol), diphenylacetylene (1.96 g, 11 mmol), PCl₃ (1.8 mL, 20 mmol) and *in-situ* generated 4-methoxyphenyllithium from 4-bromoanisole (0.94 g, 5.0 mmol) and *t*-BuLi (1.58 M solution in pentane, 6.3 mL, 10 mmol) in dry THF (10 mL) in the similar manner as described for **2**. *In this synthesis, the solution of the mixture containing in-situ generated 1-chloro-2,3,4,5tetraphenylphosphole was added into asolution of 4-methoxyphenyllithium in THF.* After separation by column chromatography (10/1 CHCl₃/AcOEt, $R_f = 0.14$), 1.13 g of **4** (2.2 mmol, 44% yield) was obtained as yellowish green solids: mp 270–271 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.82 (s, 3H), 6.91–6.98 (m, 6H), 7.07–7.17 (m, 16H), 7.83–7.88 (m, 2H). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 45.12. HRMS Calcd for C₃₅H₂₇O₂P: 510.1749. Found: 510.1752.

2,3,4,5-Tetraphenyl-1-(4'-trifluoromethylphenyl)-1*H*-phosphole-1-oxide (5). This compound was prepared from lithium (granular, 138 mg, 20 mmol), diphenylacetylene (3.74 g, 21 mmol), PCl₃ (3.5 mL, 40 mmol) and *in-situ* generated 4-methoxyphenyllithium from 4-trifluoromethyl-1-bromobenzene (2.2 g, 10 mmol) and *n*-BuLi (1.60 M solution in hexane, 12.5 mL, 10 mmol) in dry Et₂O (10 mL) in the similar manner as described for **2**. In this reaction, *m*-CPBA (3.36 g, 15 mmol) was used as an oxidant instead of H₂O₂. After separation by column chromatography (20/1 CHCl₃/AcOEt, $R_f = 0.41$), 1.04 g of **5** (1.89 mmol, 19% yield) was obtained as yellow solids: mp 283–284 °C. ¹H NMR (CDCl₃, 400 MHz) δ 6.92–6.94 (m, 4H), 7.07–7.22(m, 16H), 7.72 (dd, J = 8.0 Hz, 1.6 Hz, 4H), 8.04–8.09 (m, 2H). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 43.00. HRMS Calcd for C₁₆H₂₆O₂: 548.1517. Found: 548.1516.

2. NMR Spectra



Figure S1. ¹H NMR spectrum of **1**.



Figure S2. ${}^{31}P{}^{1}H$ NMR spectrum of 1.



Figure S3. ¹H NMR spectrum of **2**.



Figure S4. ${}^{31}P{}^{1}H$ NMR spectrum of 2.



Figure S5. ¹H NMR spectrum of **3**.



Figure S6. ${}^{31}P{}^{1}H$ NMR spectrum of 3.



Figure S7. ¹H NMR spectrum of **4**.



Figure S8. ${}^{31}P{}^{1}H$ NMR spectrum of 4.



Figure S9. ¹H NMR spectrum of **5**.



Figure S10. ¹⁹F NMR spectrum of **5**.



Figure S11. ${}^{31}P{}^{1}H$ NMR spectrum of 5.

3. X-ray Crystallographic Analysis

X-ray crystallographic analyses were performed for 1-aryl-2,3,4,5-tetraphenylphosphole oxides **2–5**. The crystallographic data are summarized below and are available as CIF files from Cambridge Crystallographic Database Centre (CCDC) on quoting the depository numbers 767155, 767156, 767157, and 767158, for **2**, **3**, **4**, and **5**, respectively. The crystallographic data obtained for pentaphenylphosphole oxide **1** was identical with that reported in literature.³ Crystal packing structures for compounds **2–5** are shown in Figures S15–18.

X-ray Crystallographic Analysis of 2. Single crystals of **2** suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of **2** in chloroform. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71070$ Å) and graphite monochromator. A total of 23470 reflections were measured at a maximum 2 θ angle of 50.0°, of which 4931 were independent reflections ($R_{int} = 0.0628$). The structure was solved by direct method (SIR97)⁴ and refined by the full-matrix least-squares on F^2 (SHELXL-97).⁵ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: Formula $C_{37}H_{31}OP$; FW = 522.59. crystal size 0.15 mm × 0.10 mm × 0.05 mm, monoclinic, $P2_1/n$ (#14), a = 10.1486(8) Å, b = 16.5262(11) Å, c = 17.1966(14) Å, $\beta = 97.0498(14)^\circ$, V = 2862.4(4) Å³, Z = 4, $D_{caled} = 1.213$ g cm⁻³, $\mu = 0.124$ mm⁻¹; $R_1 = 0.0580$ ($I > 2\sigma(I)$), $wR_2 = 0.1160$ (all data), GOF = 1.171.

X-ray Crystallographic Analysis of 3. Single crystals of **3** suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of **3** in chloroform. Intensity data were collected at 100 K on a Rigaku Single Crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71070$ Å) and graphite monochromator. A total of 28731 reflections were measured at a maximum 2θ angle of 50.0°, of which 5979 were independent reflections ($R_{int} = 0.0374$). The structure was solved by direct method (SIR97)⁴ and refined by the full-matrix least-squares on F^2 (SHELXL-97).⁵ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: Formula C₄₃H₄₃OP; FW = 606.74. crystal size 0.15 mm × 0.05 mm, orthorhombic, $P2_12_12_1$ (#19), a = 9.153(3) Å, b = 10.506(4) Å, c = 35.335(12) Å, V = 3398.1(19) Å³, Z = 4, $D_{calcd} = 1.186$ g cm⁻³, $\mu = 0.113$ mm⁻¹; $R_1 = 0.0312$ ($I > 2\sigma(I)$), $wR_2 = 0.0725$ (all data), GOF = 1.085, Flack parameter =

0.07(7).

X-ray Crystallographic Analysis of 4. Single crystals of **4** suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of **4** in chloroform. Intensity data were collected at 100 K on a Rigaku Single Crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71070$ Å) and graphite monochromator. A total of 9049 reflections were measured at a maximum 2θ angle of 50.0°, of which 4624 were independent reflections ($R_{int} = 0.0279$). The structure was solved by direct method (SIR97)⁴ and refined by the full-matrix least-squares on F^2 (SHELXL-97).⁵ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: Formula C₃₅H₂₇O₂P; FW = 510.54. crystal size 0.20 mm × 0.20 mm × 0.20 mm, triclinic, *P*-1 (#2), *a* = 10.234(3) Å, *b* = 10.522(2) Å, *c* = 14.911(5) Å, $\alpha = 70.376(11)^\circ$, $\beta = 89.627(14)^\circ$, $\gamma = 63.750(10)^\circ$, V = 1337.0(6) Å³, *Z* = 2, $D_{caled} = 1.268$ g cm⁻³, $\mu = 0.134$ mm⁻¹; $R_1 = 0.0415$ ($I > 2\sigma(I)$), $wR_2 = 0.1096$ (all data), GOF = 1.075.

X-ray Crystallographic Analysis of 5. Single crystals of 5 suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of 5 in chloroform. Intensity data were collected at 84 K on a Rigaku Single Crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71070$ Å) and graphite monochromator. A total of 17965 reflections were measured at a maximum 2 θ angle of 50.0°, of which 4724 were independent reflections ($R_{int} = 0.0790$). The structure was solved by direct method (SIR97)⁴ and refined by the full-matrix least-squares on F^2 (SHELXL-97).⁵ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: Formula C₃₅H₂₄ F₃OP; FW = 548.51. crystal size 0.25 mm × 0.01 mm × 0.01 mm, monoclinic, $P2_1/c$ (#14), a = 6.2429(16) Å, b = 21.249(5) Å, c = 20.413(5) Å, $\beta = 97.4377(14)^\circ$, V = 2685.1(11) Å³, Z = 4, $D_{calcd} = 1.357$ g cm⁻³, $\mu = 0.151$ mm⁻¹; $R_1 = 0.0775$ ($I > 2\sigma(I)$), $wR_2 = 0.1761$ (all data), GOF = 1.098.



Figure S12. ORTEP drawing of **3** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.



Figure S13. ORTEP drawing of 4 (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.



Figure S14. ORTEP drawing of 5 (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.



Figure S15. Crystal packing structure of **2** along *a* axis (white, carbon; red, oxygen; orange, phosphorus). Hydrogen atoms are omitted for clarity.



Figure S16. Crystal packing structures of **3** along (a) *a* axis and (b) *b* axis (white, carbon; red, oxygen; orange, phosphorus). Hydrogen atoms are omitted for clarity.





Figure S17. Crystal packing structures of 4 along (a) b axis and (b) c axis (white, carbon; red, oxygen; orange, phosphorus). Hydrogen atoms are omitted for clarity.



Figure S18. Crystal packing structure of **5** along *a* axis (white, carbon; red, oxygen; green, fluorine; orange, phosphorus). Hydrogen atoms are omitted for clarity.

4. Photophysical Properties

Measurements of Solution Samples. UV-visible absorption spectra were recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Steady-state fluorescence spectra of sample solutions were recorded on a F-4500 Hitachi spectrometer with a resolution of 1 nm. Spectral grade THF was deaerated by purging with an argon gas stream at least for 30 min before measurement. The sample solutions of ca. 10^{-5} M in a 1 cm square quartz cell were used. For the fluorescence measurement, the sample solutions were excited at the absorption maximum wavelengths for each compounds. UV-Vis absorption and fluorescence spectra of compounds **1–5** in THF are shown in Figures S19–23.



Figure S19. UV-Vis absorption and fluorescence spectra (excited at 387 nm) of 1 in THF.



Figure S20. UV-Vis absorption and fluorescence spectra (excited at 389 nm) of 2 in THF.



Figure S21. UV-Vis absorption and fluorescence spectra (excited at 391 nm) of 3 in THF.



Figure S22. UV-Vis absorption and fluorescence spectra (excited at 388 nm) of 4 in THF.



Figure S23. UV-Vis absorption and fluorescence spectra (excited at 389 nm) of 5 in THF.

Cmpd	Absorption			Fluorescence			Stokes shift	
	$\lambda_{ m abs}$ /nm	(v_{abs}/cm^{-1})	$\log \varepsilon$	$\lambda_{\rm em}/r$	m (v_{em}	$n/cm^{-1})$	FWHM / cm ⁻¹	/ cm ⁻¹
1	387	25800	3.92	520	1	9200	6100	6600
2	389	25700	3.85	517	19	9300	5100	6400
3	391	25600	3.90	509	1	9600	4700	6000
4	388	25800	3.91	517	1	9300	5500	6500
5	389	25700	3.89	528	1	8900	5100	6800

Table S1. Photophysical Data for 1-Aryl-2,3,4,5-tetraphenylphosphole Oxides in THF

Measurements of Fluorescence Properties in Crystal. The measurements of fluorescence spectra and the determination of absolute fluorescence quantum yields ($\Phi_{\rm F}$) in crystalline state were conducted with a Hamamatsu C9920-02 calibrated integrating sphere system equipped with multichannel spectrometer (PMA-11). Time-resolved fluorescence fluorescence measured with a Hamamatsu Picosecond Fluorescence Measurement System C4780 equipped with a USHO pulsed nitrogen laser (excitation wavelength 337 nm with a repetition rate of 10 Hz). Regarding the size dependency of the $\Phi_{\rm F}$ described in a recent literature,⁶ we evaluated the $\Phi_{\rm F}$ and $\tau_{\rm s}$ of single crystals in various different sizes. The absolute fluorescence quantum yield measurements for the crystalline samples were

performed using several pieces of crystals for each measurement on a quartz dish. Since it was quite difficult to separate the crystals in size completely, the crystals used for each measurement have a certain size distribution. The measurements showed a slight variation in the $\Phi_{\rm F}$ values dependent on the size distribution of the crystals. Tables S2–S8 summarize the $\Phi_{\rm F}$ values for several measurements for each compound. The approximate size ranges given in Table S9 are those afforded the highest $\Phi_{\rm F}$ value for each compound. Since we used the crystalline sample without any mechanical milling process, we assume that the reabsorption of the fluorescence is a major factor for the variation in the $\Phi_{\rm F}$. The larger crystals should cause the larger extent of reabsorption. Therefore, we adopted the highest values among several measurements as an inherent $\Phi_{\rm F}$ value in the crystalline state. Table S9 summarizes the typical sizes of crystals and the corresponding values of $\Phi_{\rm F}$ and $\tau_{\rm s}$ for compounds 1–7. The fluorescence spectra of compounds 1–5 in the crystals are shown in Figure S24. The fluorescence data for compounds 1–7 are summarized in Table S8. All the decay profiles were fitted reasonably well using a single exponential function except for 7, as shown in Figures 25–31.

entry	crystal size / mm ^a	${oldsymbol{\varPhi}_{ extsf{F}}}^{b}$	$ au_{ m s}$ / ns ^c
1	$0.80 \times 0.20 \times 0.20 - 2.0 \times 0.50 \times 0.20$	0.35	d
2	$<0.10 \times 0.01 \times 0.01 - 0.70 \times 0.30 \times 0.05$	0.49	5.0
3	$0.10 \times 0.01 \times 0.01 - 0.80 \times 0.40 \times 0.10$	0.49	d
4	$0.10 \times 0.01 \times 0.01 - 1.0 \times 0.40 \times 0.10$	0.48	d
5	$0.80 \times 0.20 \times 0.20 - 2.0 \times 0.50 \times 0.20$	0.35	d

Table S2. Fluorescence Data for 1 in Crystalline State

^{*a*}Observed values using optical microscope. ^{*b*}Absolute quantum yield determined by a calibrated integrating sphere system equipped with multichannel spectrometer. ^{*c*}Fluorescence lifetime. ^{*d*}Not measured.

Table S3. Fluorescence Data	1 for 2 in	Crystalline	State
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entry	size / mm ^a	${oldsymbol{\varPhi}_{ extsf{F}}}^{b}$	$ au_{ m s}$ / ns c
1	$0.1 \times 0.1 \times 0.1$	0.75	d
2	$0.1 \times 0.1 \times 0.1 - 0.5 \times 0.4 \times 0.3$	0.89	d
3	$0.01 \times 0.01 \times 0.01 - 0.50 \times 0.30 \times 0.10$	0.91	10.6

^aObserved values using optical microscope. ^bAbsolute quantum yield determined by a

calibrated integrating sphere system equipped with multichannel spectrometer. ^cFluorescence lifetime. ^dNot measured.

entry	size / mm^a	${oldsymbol{\Phi}_{ extsf{F}}}^{b}$	$ au_{ m s}$ / ns ^c
1	$0.30 \times 0.20 \times 0.10 - 1.3 \times 0.50 \times 0.10$	0.74	d
2	$0.20 \times 0.10 \times 0.10 - 0.50 \times 0.20 \times 0.10$	0.70	d
3	$0.10 \times 0.10 \times 0.02 - 0.70 \times 0.30 \times 0.03$	0.75	10.0

Table S4. Fluorescence Data for 3 in Crystalline State

^{*a*}Observed values using optical microscope. ^{*b*}Absolute quantum yield determined by a calibrated integrating sphere system equipped with multichannel spectrometer. ^{*c*}Fluorescence lifetime. ^{*d*}Not measured.

Table S5. Fluorescence Data for 4 in Crystalline State

entry	size / mm ^a	${oldsymbol{\Phi}_{ extsf{F}}}^{b}$	$ au_{ m s}$ / ns ^c
1	$0.80 \times 0.50 \times 0.50 - 1.7 \times 0.80 \times 0.50$	0.83	d
2	$0.20 \times 0.20 \times 0.10 - 0.50 \times 0.30 \times 0.20$	0.89	d
3	$0.10 \times 0.10 \times 0.10 - 0.30 \times 0.20 \times 0.20$	0.91	10.7

^{*a*}Observed values using optical microscope. ^{*b*}Absolute quantum yield determined by a calibrated integrating sphere system equipped with multichannel spectrometer. ^{*c*}Fluorescence lifetime. ^{*d*}Not measured.

Table S6. Fluorescence Data for 5 in Crystalline State

entry	size / mm ^a	${oldsymbol{\Phi}_{\! m F}}^b$	$ au_{ m s}$ / ns ^c
1	$1.0 \times 0.01 \times 0.01 - 4.0 \times 0.20 \times 0.20$	0.25	d
2	$0.60 \times 0.01 \times 0.01 - 3.0 \times 0.20 \times 0.10$	0.25	3.1
3	$0.50 \times 0.01 \times 0.01 - 2.6 \times 0.10 \times 0.07$	0.24	d

^{*a*}Observed values using optical microscope. ^{*b*}Absolute quantum yield determined by a calibrated integrating sphere system equipped with multichannel spectrometer. ^{*c*}Fluorescence lifetime. ^{*d*}Not measured.

entry	size / mm^a	${oldsymbol{\varPhi}_{ extsf{F}}}^{b}$	$ au_{ m s}$ / ns c
1	$0.80 \times 0.80 \times 0.80 - 2.0 \times 1.5 \times 1.5$	0.24	d
2	$0.30 \times 0.20 \times 0.20 - 0.90 \times 0.80 \times 0.50$	0.33	2.6
3	$0.15 \times 0.10 \times 0.10 - 1.0 \times 1.0 \times 0.80$	0.32	d

Table S7. Fluorescence Data for 6 in Crystalline State

^{*a*}Observed values using optical microscope. ^{*b*}Absolute quantum yield determined by a calibrated integrating sphere system equipped with multichannel spectrometer. ^{*c*}Fluorescence lifetime. ^{*d*}Not measured.

Table S8. Fluorescence Data for 7 in Crystalline State

entry	size / mm ^a	${oldsymbol{\Phi}_{ extsf{F}}}^{b}$	$ au_{ m s}$ / ns ^c
1	$0.2 \times 0.1 \times 0.01 - 3.0 \times 1.5 \times 0.03$	0.68	d
2	$0.2 \times 0.08 \times 0.01 - 0.5 \times 0.2 \times 0.02$	0.75	d
3	$0.2 \times 0.08 \times 0.01 - 1.0 \times 0.4 \times 0.02$	0.76	0.74 / 8.3

^{*a*}Observed values using optical microscope. ^{*b*}Absolute quantum yield determined by a calibrated integrating sphere system equipped with multichannel spectrometer. ^{*c*}Fluorescence lifetime. ^{*d*}Not measured.

Table S9. Fluorescence Data of 1–7 in the Crystalline State

cmpd	approximate crystal size / mm ^a	${oldsymbol{\varPhi}_{\mathrm{F}}}^a$	$ au_{ m s}$ / ns	$k_{\rm r}$ / ${\rm s}^{-1}$	$k_{\rm nr} / {\rm s}^{-1}$
1	$0.10 \times 0.01 \times 0.01 - 0.70 \times 0.30 \times 0.05$	0.49	5.0	9.8×10^{7}	1.0×10^{8}
2	$0.01 \times 0.01 \times 0.01 - 0.50 \times 0.30 \times 0.10$	0.91	10.6	8.6×10^{7}	8.2×10^{6}
3	$0.10 \times 0.10 \times 0.02 - 0.70 \times 0.30 \times 0.03$	0.75	10.0	7.4×10^{7}	2.6×10^{7}
4	$0.10 \times 0.10 \times 0.10 - 0.30 \times 0.20 \times 0.20$	0.91	10.7	8.5×10^{7}	8.1×10^{6}
5	$0.60 \times 0.01 \times 0.01 - 3.0 \times 0.20 \times 0.10$	0.25	3.1	8.0×10^{7}	2.4×10^{8}
6	$0.30 \times 0.20 \times 0.20 - 0.90 \times 0.80 \times 0.50$	0.33	2.6	1.3×10^{8}	2.6×10^{8}
7	$0.2 \times 0.08 \times 0.01 - 1.0 \times 0.4 \times 0.02$	0.76	5.7	_	—

^{*a*}Approximate sizes range determined using optical microscope. ^{*b*}Absolute quantum yield determined by a calibrated integrating sphere system equipped with multichannel spectrometer. ^{*c*}Fluorescence lifetime. ^{*d*}Not measured. ^{*c*}Radiative rate constant: $k_r = \Phi_F / \tau_s$. ^{*d*}Non-radiative rate constant: $k_{nr} = (1 - \Phi_F) / \tau_s$.



Figure S24. Fluorescence spectra of 1–5 in the crystalline state (excited at 340 nm). The fluorescence intensities were normalized to unity.



Figure S25. Fluorescence decay profiles of **1** in the crystalline state ($\tau = 4.99$ ns, $A_1 = 0.690$, $\chi^2 = 1.014$). IRF represents the instrumental response.



Figure S26. Fluorescence decay profiles of **2** in the crystalline state ($\tau = 10.6 \text{ ns}, A_1 = 0.756$, $\chi^2 = 1.158$). IRF represents the instrumental response.



Figure S27. Fluorescence decay profiles of **3** in the crystalline state ($\tau = 10.0 \text{ ns}, A_1 = 0.705$, $\chi^2 = 1.077$). IRF represents the instrumental response.



Figure S28. Fluorescence decay profiles of **4** in the crystalline state ($\tau = 10.7 \text{ ns}$, $A_1 = 0.126$, $\chi^2 = 1.176$). IRF represents the instrumental response.



Figure S29. Fluorescence decay profiles of **5** in the crystalline state ($\tau = 3.06 \text{ ns}, A_1 = 0.863$, $\chi^2 = 1.133$). IRF represents the instrumental response.



Figure S30. Fluorescence decay profiles of **6** in the crystalline state ($\tau = 2.63$ ns, $A_1 = 0.128$, $\chi^2 = 1.021$). IRF represents the instrumental response.



Figure S31. Fluorescence decay profiles of 7 in the crystalline state ($\tau_1 = 0.74$ ns, $\tau_2 = 8.32$ ns, $A_1 = 0.5914$, $A_2 = 3.338$, $\chi^2 = 1.000$). IRF represents the instrumental response.

Measurements of Fluorescence Properties in PMMA matrices. For the measurements in polymer matrix, the samples were prepared by casting of a THF (spectral grade) solution of a mixture of 1-aryl-2,3,4,5-tetraphenylphosphole oxides (1 mg/mL) and poly(methyl metacrylate) (PMMA) (0.1 g/mL) on a quartz plate. For the measurements of fluorescence spectra and the determination of the absolute quantum yields in PMMA matrix, a Hamamatsu C9920-02 calibrated integrating sphere system equipped with multichannel spectrometer (PMA-11) was used. Time-resolved fluorescence spectra were measured with a Hamamatsu Picosecond Fluorescence Measurement System C4780 equipped with a Hamamatsu PLP-10 picosecond light pulser (excitation wavelength 375 nm with a repetition rate of 10 Hz) or USHO nitrogen laser (excitation wavelength 337 nm with a repetition rate of 10 Hz). We confirmed a negligible concentration dependence of the Φ_F of **2** in the PMMA matrices in the concentration range of 0.5–1wt%.



Figure S32. Fluorescence spectrum of 1 in a PMMA matrix.



Figure S33. Fluorescence spectrum of 2 in a PMMA matrix.



Figure S34. Fluorescence spectrum of **3** in a PMMA matrix.



Figure S35. Fluorescence spectrum of 4 in a PMMA matrix.



Figure S36. Fluorescence spectrum of **5** in a PMMA matrix.

5. References

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