

Supporting information for

Radioluminescence from thermally activated delayed fluorescent molecules doped P-dots

Daiki Asanuma,^{a,†} Hieu Thi Minh Nguyen,^{b,†} Zuoyue Liu,^a Sachiko Tojo,^a Hajime Shigemitsu,^c Minoru Yamaji,^d Kiyohiko Kawai,^{a,e} Tadashi Mori,^c Toshiyuki Kida,^c Guillem Pratx,^{b,*} Mamoru Fujitsuka,^{a,f,*} and Yasuko Osakada^{a,f,g,*}

† Equally contributed to this work

E-mail: yosakada@sanken.osaka-u.ac.jp (Y.O.).

- a. SANKEN, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047 (Japan).
- b. Department of Radiation Oncology and Medical Physics, Stanford University, 300 Pasteur Dr., Stanford, CA 94305 (USA).
- c. Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, (Japan).
- d. Division of Molecular Science, Graduate School of Science and Engineering, Gunma University, Ota, Gunma 373-0057 (Japan).
- e. Department of Life Science and Technology, Tokyo Institute of Technology, B-52, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8501, (Japan).
- f. Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, (Japan).
- g. Institute for Advanced Co-Creation Studies, Osaka University, Yamadagaoka 1-1, Suita, Osaka 565-0871 (Japan).

Materials and methods.

Polyvinylcarbazole (PVK) was purchased from Sigma aldrich. (St. Louis, Missouri, United States). PVA and 10-[4-[4,6-Di(adamantan-1-yl)-1,3,5-triazin-2-yl]phenyl]-9,9-diphenyl-9,10-dihydroacridine (PA-TA) and 10-[4-[4,6-Di(adamantan-1-yl)-1,3,5-triazin-2-yl]phenyl]-9,9-dimethyl-9,10-dihydroacridine (MA-TA) were purchased from TCI (Tokyo, Japan.). PEG polymer was purchased from polymer source (Quebec, Canada). Tetrahydrofuran (THF) was purchased from FUJIFILM Wako (Osaka, Japan). All chemicals were used as received without any further purification.

General characterization.

Absorption spectra were measured at room temperature using a V630 UV-visible spectrophotometer (JASCO, Tokyo, Japan). Emission spectra were measured at room temperature using an FP-8200 fluorescence spectrometer (JASCO, Tokyo, Japan). The hydrodynamic diameter of P-dots was measured by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Panalytical, UK). The morphology of P-dots particles was observed using an ultra-high resolution analytical electron microscope JEM-ARM200F (JEOL, Tokyo, Japan). For sample preparation, the synthesized P-dots were sonicated for 1 minute and 20 μ L of sample solution was dropped onto a polymer coated Cu grid. After drying completely, they were hydrophilized for 60 s using the HDT-400 hydrophilic treatment system (JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) measurements were taken. For particle size analysis, 100 particles were extracted from the resulting TEM images and analyzed using ImageJ software manually. Quantum yields of

photoluminescence were measured using a Quantaaurus-QY absolute PL quantum yield measurement system (HAMAMATSU Photonics K.K., Shizuoka, Japan) at an excitation wavelength of 355 nm. Measurements were performed under aerobic and degassing conditions. The sample degassing for each measurement was performed by argon bubbling for 10 minutes.

Synthesis of P-dots.

TADF molecule-doped P-dots were synthesized according to the precipitation method described by us previously with slight modifications.¹ PVK and PEG-COOH polymers and TADF molecules were each dissolved (1.0 mg/mL) in THF to prepare stock solutions (Table S1). Each stock solution was mixed with 30 μ L, 60 μ L, and 150 μ L each and diluted with 60 μ L of THF. Under sonication, the mixed solution was dispersed in 1 mL of milliQ water and sonicated additionally for 5 minutes. THF was then removed by centrifugal evaporation and water was added to synthesize a total of 1 mL of aqueous P-dots solution. To 1 mL of the synthesized P-dots solution, 0.10 g of sucrose was added and completely dissolved. The mixed solution was frozen in liquid nitrogen (-195.8°C) and lyophilized using a freeze dryer (EYELA, Tokyo, Japan) for X-ray imaging experiments.

Fabrication of P-dots film

The polymer matrix and P-dots solution were mixed, and the water was evaporated in an oven to synthesize the film. For the matrix, 2.0 g PVA ($n = 1700$) was dissolved in 20 mL purified water and heated and stirred at 120°C for 30 min. The matrix was then prepared by adding 1.0 mL of PEG ($M_w = 200$) and heating and stirring at 90°C for 30 min. For P-dots,

10 mL of the synthesized P-dots sample was transferred to a tube for spin column (VIVASPIN TURBO15 50 mL 10k), centrifuged at 3000 g for 8 min at 15°C, and concentrated to a total volume of 0.50 mL (20 x concentration). They were mixed with matrix and concentrated P-dots at a 1:1 ratio in 1.5 mL tube. 0.25 mL of the mixture was dropped into a plastic petri dish and dried at 50°C. Five films were then laminated together to form a thick (1.5 mm) film with a diameter of approximately 12 mm. For comparison, films with only PEG and PVA were also fabricated.

Photoluminescent lifetime measurement.

Photoluminescence luminescence lifetime was measured at room temperature by the photon counting method using a Quantaaurus-Tau compact fluorescence lifetime measurement system C11367 (HAMAMATSU Photonics K.K., Shizuoka, Japan). Measurements were performed under aerobic and degassing conditions. Samples were prepared to have an absorbance of 1.0 at 355 nm. Curve fitting and analysis were performed using the instrument's software. Lifetimes were determined by three-component exponential curve fitting ($y = y_0 + A_1 * \exp(-x_1 / \tau_1) + A_2 * \exp(-x_2 / \tau_2) + A_3 * \exp(-x_3 / \tau_3)$, $\tau = \sum A_i \tau_i^2 / \sum A_i \tau_i$).

Laser flash photolysis experiment.

Pico second transient absorption was measured at room temperature by the RIPT method using the picosecond transient absorption spectroscopy system picoTAS (UNISOKU, Osaka, Japan). Measurements were performed under aerobic and degassing conditions. Samples were prepared to have absorbance of 1.0 at 355 nm. Curve fitting and analysis were performed using the instrument's software. Lifetimes were determined by three-component

exponential curve fitting ($y = y_0 + A_1 * \exp(-x_1 / \tau_1) + A_2 * \exp(-x_2 / \tau_2) + A_3 * \exp(-x_3 / \tau_3)$, $\tau = \Sigma A_i \tau_i^2 / \Sigma A_i \tau_i$).

Pulse radiolysis and electron beam excited photoluminescence measurements.

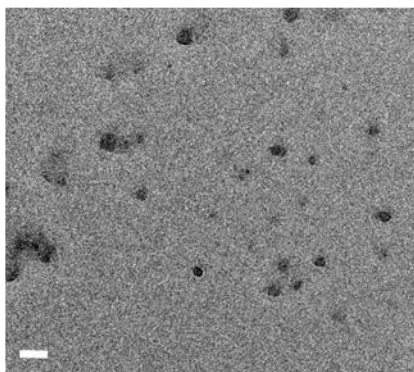
Transient absorption by the pulse radiolysis method was measured at room temperature using a multichannel spectrometer with an L-band LINAC-accelerated electron pulse (28 MeV) as the excitation source to the sample. Measurements were performed under aerobic and degassing conditions. For triplet state measurement, samples were dissolved in toluene and prepared to have an absorbance of 1.0 at 355 nm and degassed. Electron beam-induced emission spectra were measured at room temperature using a multichannel spectrometer with an L-band LINAC-accelerated electron pulse (28 MeV) as the excitation source to the sample. Measurements were performed under degassing conditions.

Hard X-ray excited luminescence measurements.

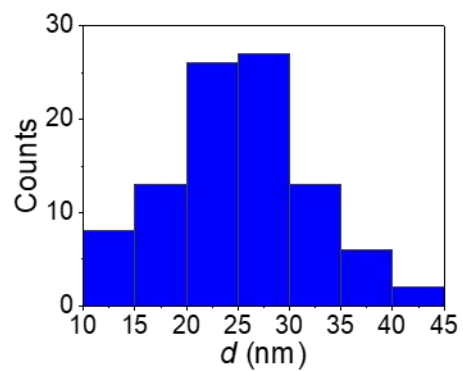
Hard X-ray excited luminescence was measured by a small animal X-ray irradiator (X-RAD SmART system, PXI, North Branford, CT, USA) and EMCCD camera placed perpendicular to the irradiation beam axis. X-ray beams (60 kVp, 20 mA, unfiltered) were collimated with a 2.5 cm diameter circular aperture and directed toward the side of a 96-well plate containing 200 μ l of sample in solution, respectively. X-ray emission images were acquired as a series of 20 frames, each with 1 s exposure, electron gain of 50, and No pixel binning was used; MATLAB (MathWorks, Natick, MA, USA) was used to remove radiation noise from the raw camera images and to quantify the image intensity. X-ray emission spectra were acquired with a separate X-ray irradiator (PXI XRAD 320, North Branford, CT, USA) and measured

with an optical spectrometer (Sensline, Avantes, Lafayette, CO, USA). X-ray beam (60 kVp, 20 mA, unfiltered) was directed at the film sample directly below the X-ray aperture to maximize the absorbed dose rate and emission intensity. The film sample was placed over the distal end of a 1 mm diameter optical fiber, with the proximal end connected to a spectrometer. Each film sample was measured three times with a 5-second exposure and averaged. The background signal (non-doped control film) was then subtracted and spectral intensity corrected to compensate for the spectrometer's non-uniform sensitivity. The spectra were then normalized and smoothed with a Savitzky-Golay filter in MATLAB.

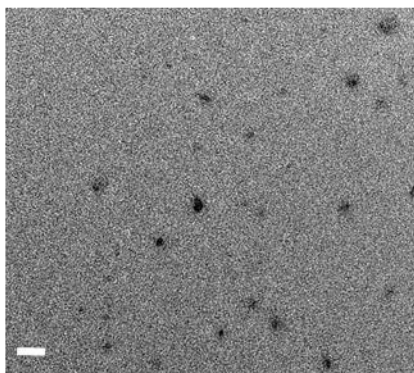
(a)



PA-TA
P-dots



(b)



MA-TA
P-dots

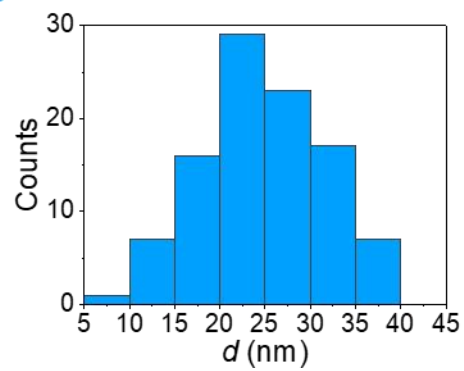


Figure S1. TEM images and histogram of their diameters for PA-TA P-dots (a) and MA-TA P-dots (b).

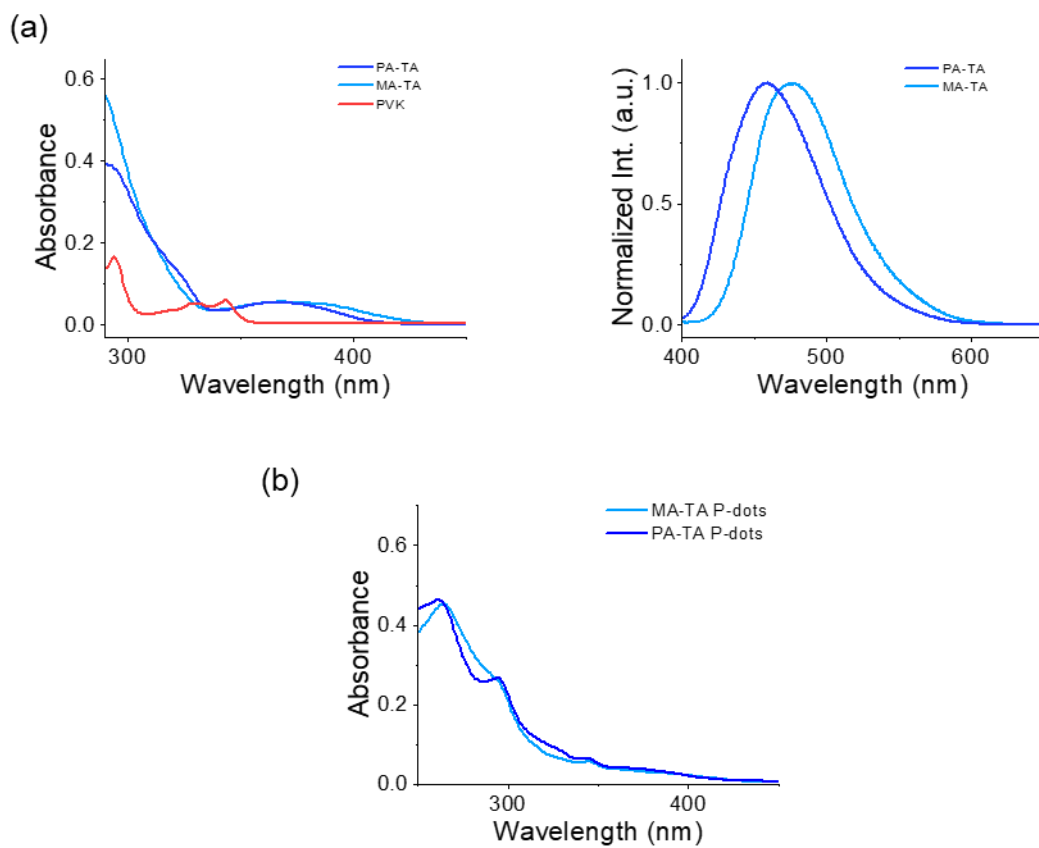


Figure S2. (a) Absorption and photoluminescence spectra of PA-TA (blue) and MA-TA (sky blue) and PVK (red) in toluene. (b) Absorption spectra of P-dots.

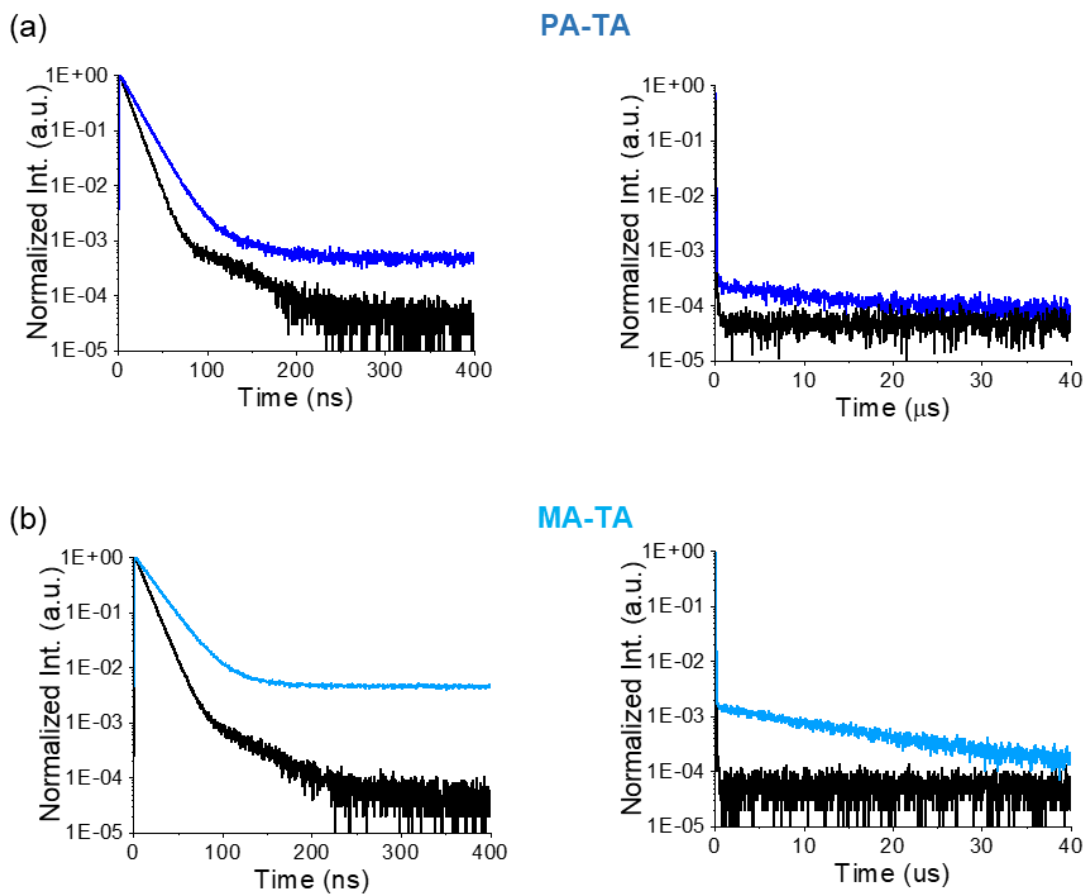


Figure S3. Photoluminescence lifetime for monomers, PA-TA (a) and MA-TA (b) in toluene under Ar (blue and sky blue) and aerated (black) condition.

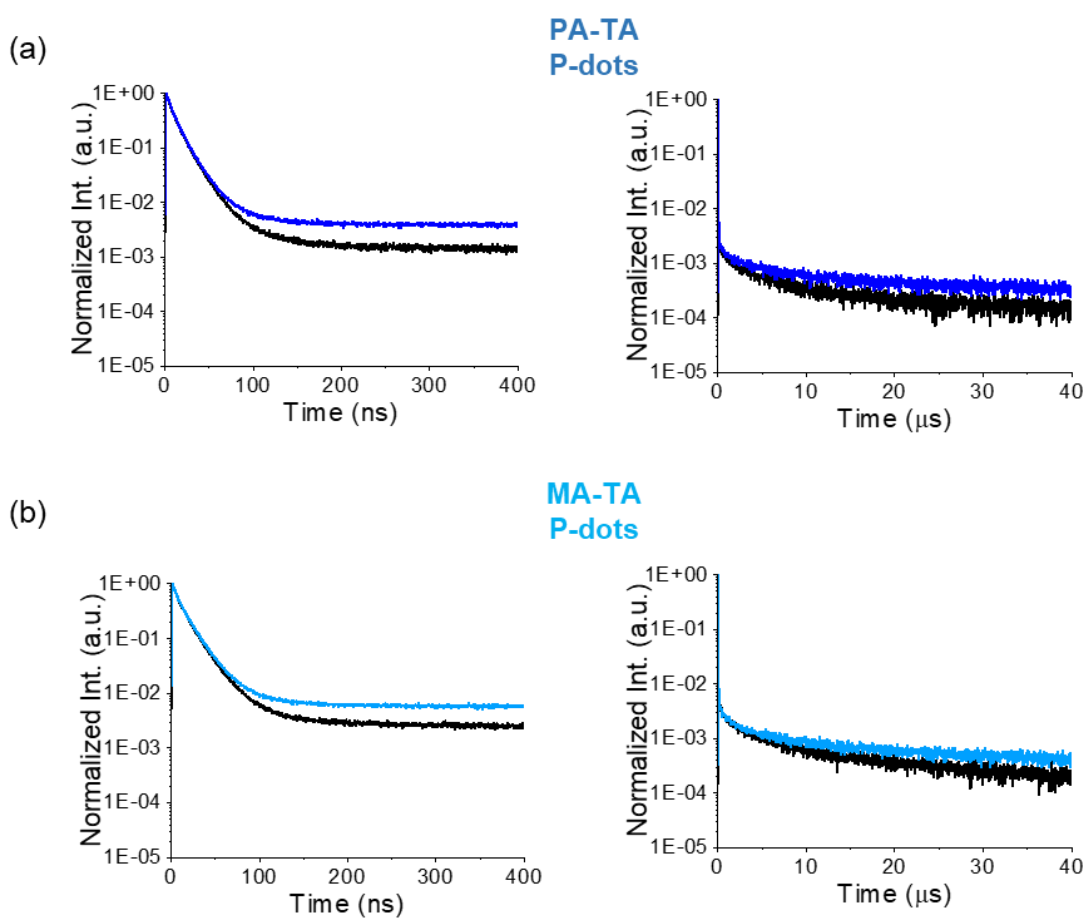


Figure S4. Photoluminescence lifetime for monomers, PA-TA P-dots (a) and MA-TA P-dots (b) in H₂O under Ar (blue and sky blue) and aerated (black) condition.

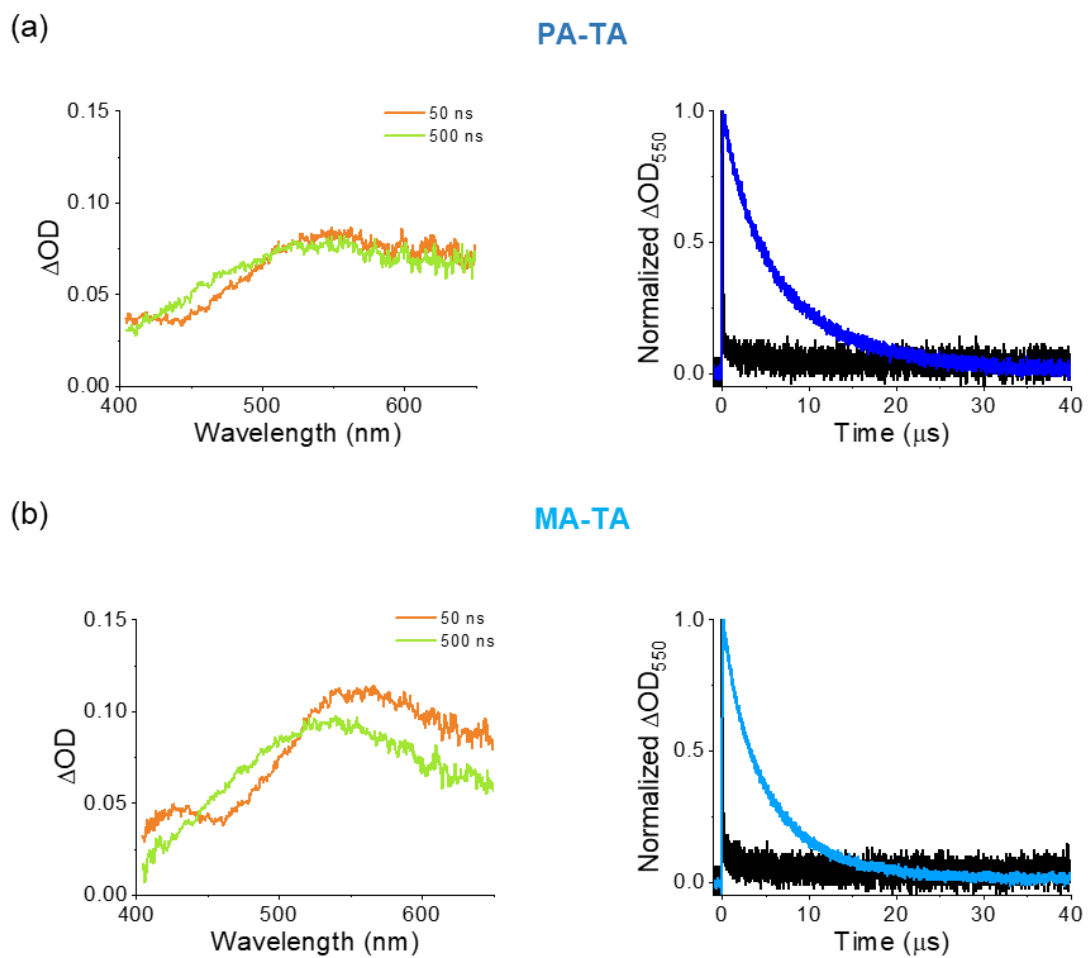


Figure S5. Transient absorption spectra and their kinetic traces obtained by pulse radiolysis for PA-TA (a) and MA-TA (b) in toluene.

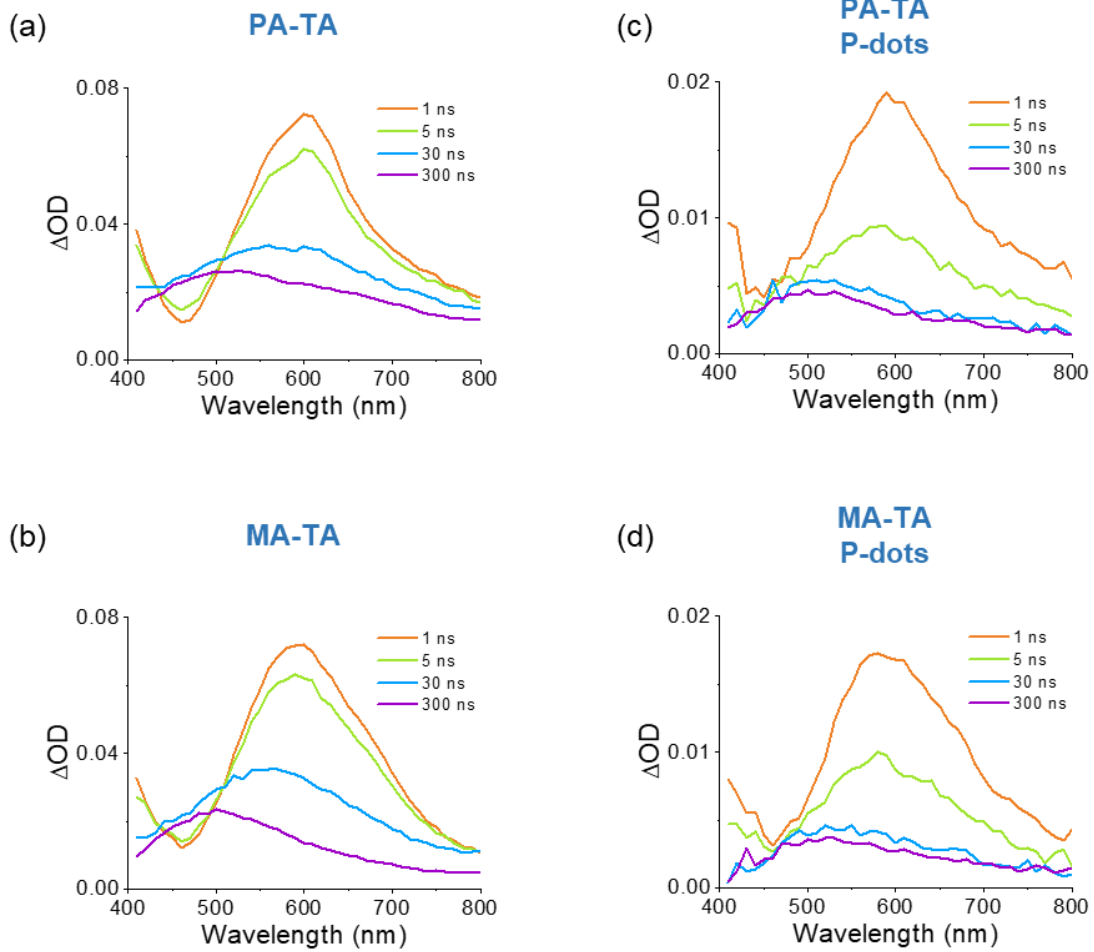


Figure S6. Transient absorption spectra for PA-TA (a), MA-TA (b) in toluene, PA-TA P-dots (c) and MA-TA P-dots (d) in H₂O.

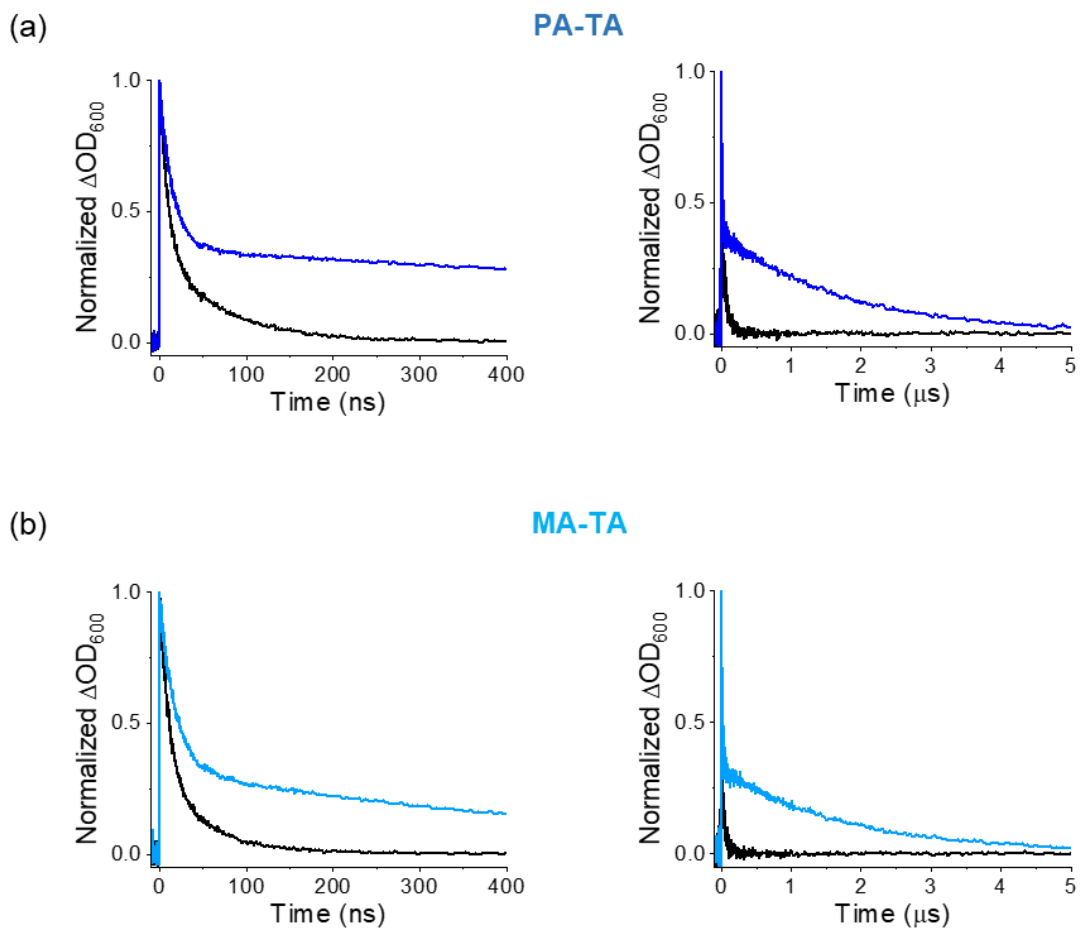


Figure S7. Kinetic traces of transient absorption at 600 nm for monomers, PA-TA (a) and MA-TA (b) in toluene under Ar (blue and sky blue) and aerated (black) condition.

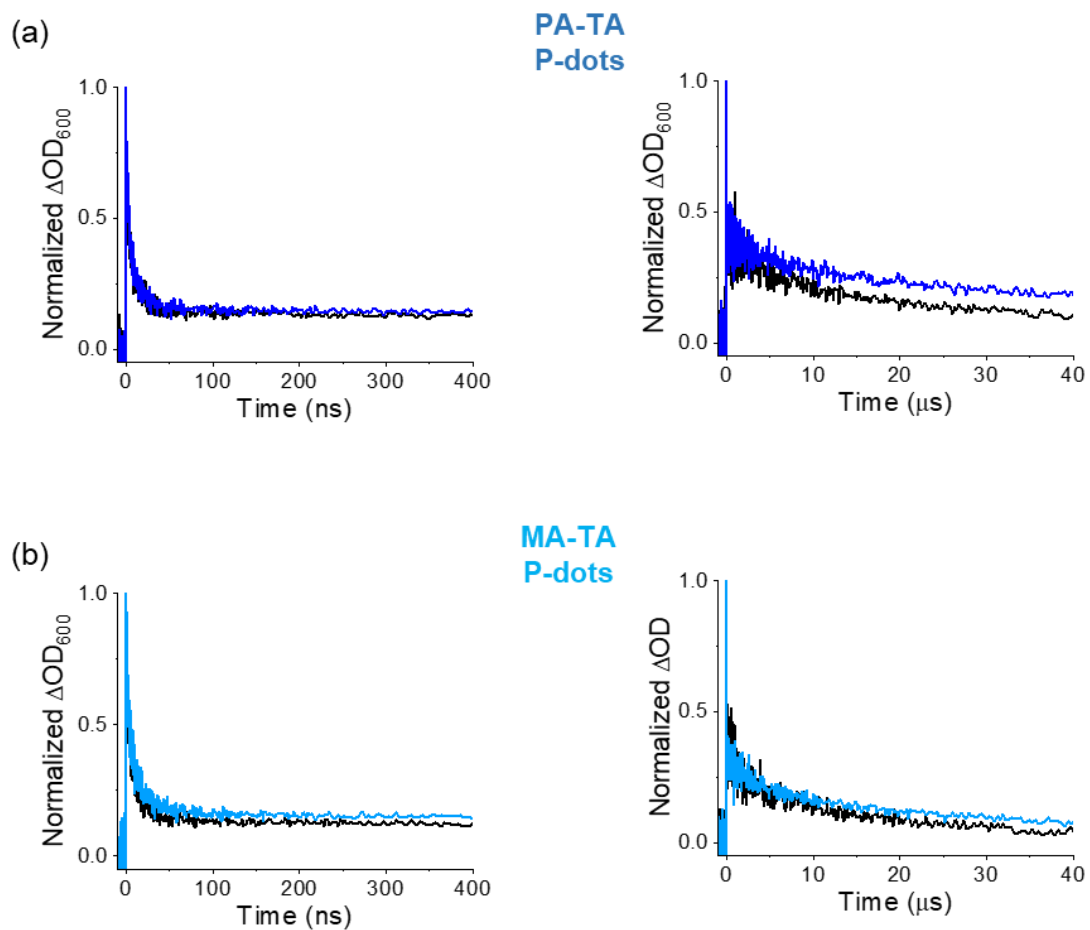


Figure S8. Kinetic traces of transient absorption at 600 nm for monomers, PA-TA P-dots (a) and MA-TA P-dots (b) in H₂O under Ar (blue and sky blue) and aerated (black) condition.

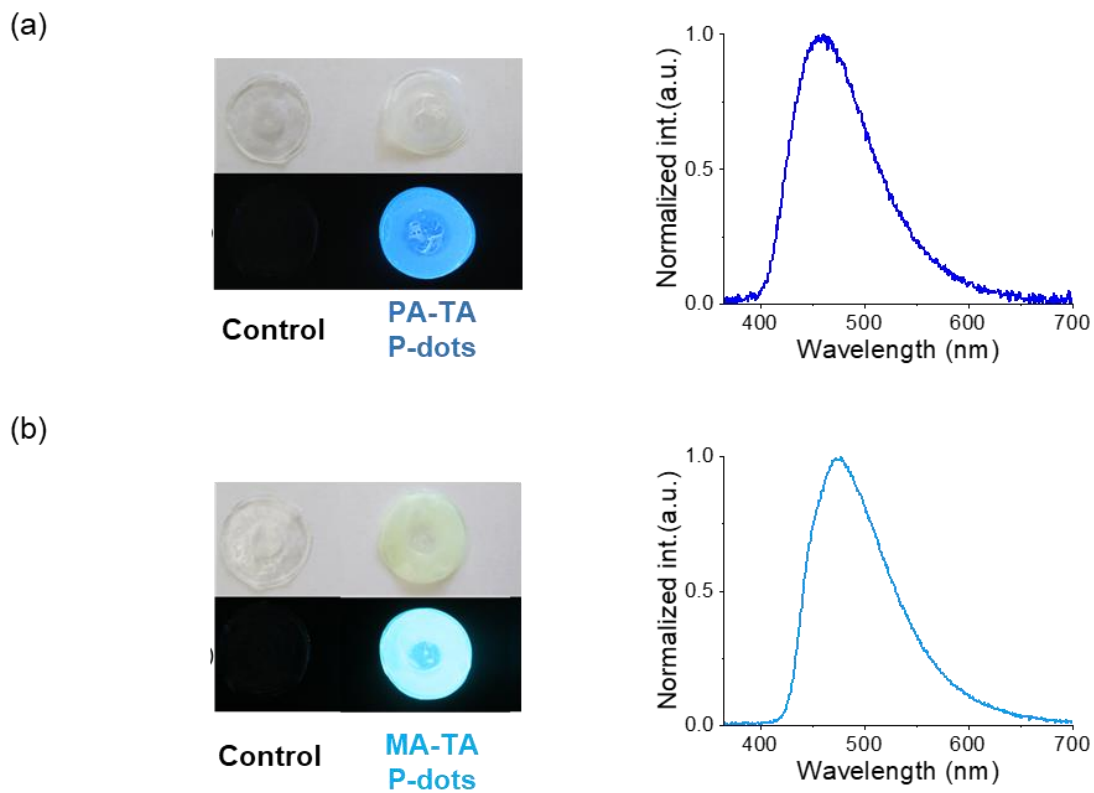


Figure S9. The photoluminescence of film embedded with PA-TA P-dots (a) and MA-TA P-dots (b). Left: photograph excited at 365 nm transilluminator, right: photoluminescence spectra.

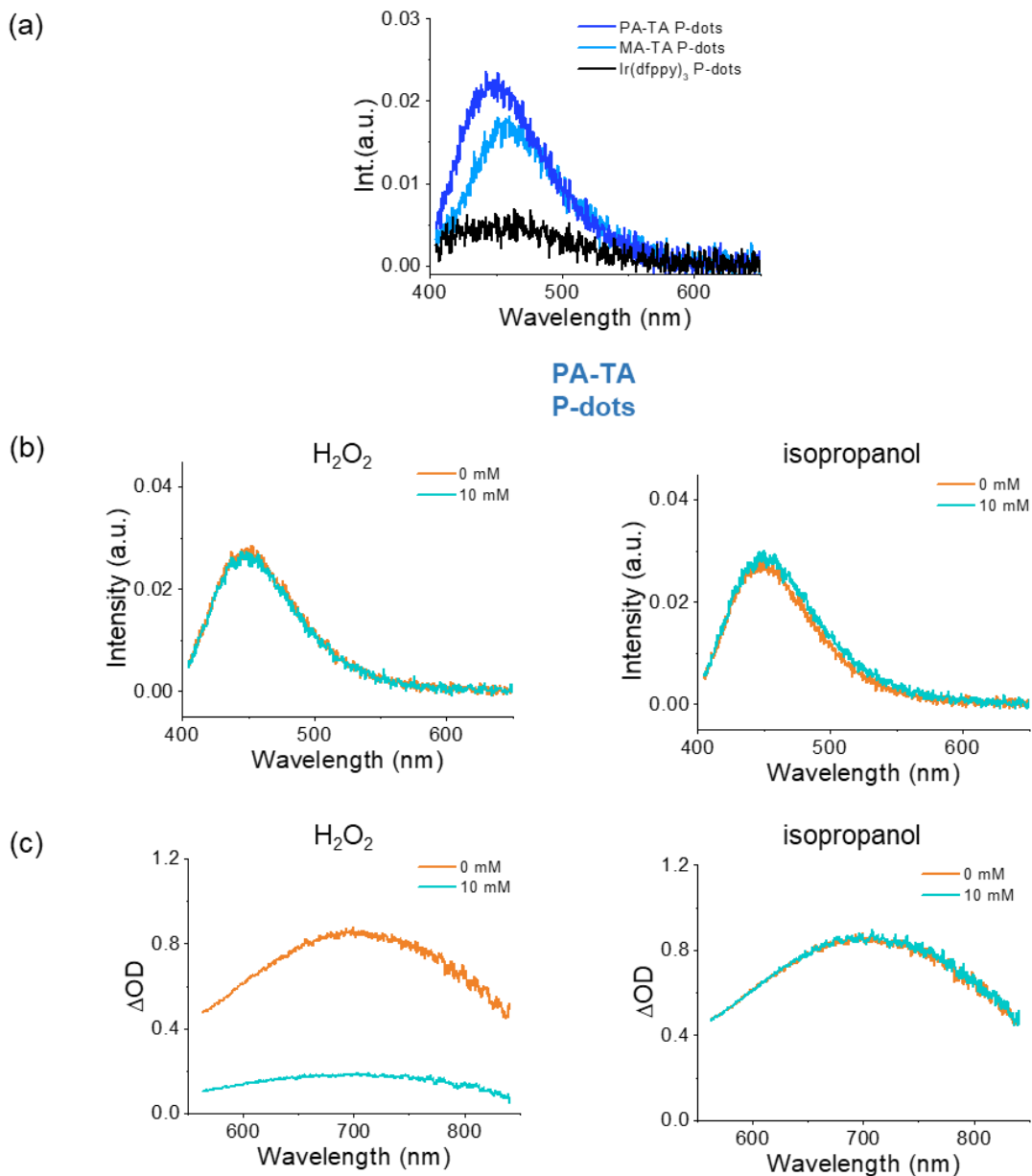


Figure S10. (a) Hard X-ray excited luminescence spectra for PA-TA and MA-TA P-dots and Ir(dfppy)₃ doped P-dots.² The normalized data is shown in Fig. 2c. (b) Hard X-ray excited luminescence of PA-TA P-dots in the presence of H₂O₂ and isopropanol.

Table S1. Volume and concentration of TADF molecules, PEG-COOH, PVK, and THF in sample preparation.

Components	Volume (μL)	Concentration ($\mu\text{g/mL}$)
TADF molecules	150	500
PEG-COOH	60	100
PVK	30	200
THF	60	
Total	300	

Table S2. The averaged sizes of P-dots measured by TEM and DLS.

Sample	Averaged size	
	TEM (nm)	DLS (nm)
PA-TA P-dots	26	73
MA-TA P-dots	25	63

Table S3. Photoluminescence absolute quantum yields for TADF monomers and P-dots.

Sample	λ_{max} (nm) ^a	<i>FWHM</i> (nm)	Φ_{PL} (Ar) ^b	Φ_{PL} (Air) ^b	Φ_{PL} (Air)/ Φ_{PL} (Ar)	Φ_{PL} (P-dots)/ Φ_{PL} (monomer)
PA-TA	456	76	0.35	0.23	0.66	-
PA-TA P-dots	456	91	0.40	0.28	0.70	1.1
MA-TA	473	72	0.35	0.19	0.54	-
MA-TA P-dots	473	81	0.44	0.32	0.73	1.4
Ir(dfppy) ₃	510	-	0.82	0.02	0.25	-
Ir(dfppy) ₃ P-dots	510	-	0.09	0.08	0.89	0.11

^a Photoluminescence λ_{max} , ^b Absolute photoluminescence quantum yields.

Table S4. Photoluminescence lifetime for TADF monomers and P-dots.

Sample	τ (μs , Ar) ^a	τ (μs , air) ^a
PA-TA	6.0	0.011
PA-TA P-dots	23	6.4
MA-TA	5.2	0.012
MA-TA P-dots	19	7.8

^a Photoluminescence lifetime determined by average of 3 components.

Table S5. Triplet lifetime and reaction rate constant with molecular oxygen determined by laser flash photolysis.

Sample	τ (μs , Ar) ^a	τ (μs , air) ^a	k_q ($\text{Lmol}^{-1}\text{s}^{-1}$) ^b
PA-TA	4.0	0.068	9.5×10^9
PA-TA P-dots	84	47	3.2×10^7
MA-TA	3.4	0.057	1.2×10^{10}
MA-TA P-dots	37	18	9.6×10^7

^a Triplet lifetime and ^b reaction rate constants determined by the equation of $k_{\text{air}} = k_{\text{Ar}} + k_q[\text{O}_2]$, $k_{\text{air}} = 1/\tau$ (air), and $k_{\text{Ar}} = 1/\tau$ (Ar). Monomers were measured in toluene ($[\text{O}_2] = 1.5 \times 10^{-3} \text{ molL}^{-1}$), and P-dots were measured in H_2O ($[\text{O}_2] = 3.0 \times 10^{-4} \text{ molL}^{-1}$).

References.

1. Y. Osakada, L. Hanson and B. Cui, *Chem. Commun.*, 2012, **48**, 3285-3287.
2. Y. Osakada, G. Prax, L. Hanson, P. E. Solomon, L. Xing and B. Cui, *Chem. Commun.*, 2013, **49**, 4319-4321.