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SUPPLEMENTAL INFORMATION

Photo-stable and highly emissive glassy organic dots exhibiting thermally activated delayed fluorescence

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Experimental Methods

1. Instruments

Absorption spectra of the samples were measured with an ultraviolet–visible–near infrared spectrometer (Lambda 950-PKA, Perkin–Elmer). Photoluminescence quantum yield was measured using a PLQY measurement system (Quantaurus-QY, Hamamatsu Photonics). The transient photoluminescence decay characteristics of samples were measured using an emission lifetime measurement system (Quantaurus-Tau, Hamamatsu Photonics). Film samples of 6 wt% 4CzIPN:mCP and pristine 4CzIPN were thermally evaporated in vacuum ($< 5.0 \times 10^{-4}$ Pa) on quartz substrates. SEM images were obtained using a JCM-5700 (JEOL) with Pt sputtered samples on a collodion-coated grid. The calorimetric characteristics were measured using the second scan of a DSC 204F1 Phoenix (NETSCH) except nanoparticle sample. All sample for DSC measurement were measured by dried powder. The melting point measurement of host matrix was performed by melting-point apparatus (M-565, Büchi). DLS measurement was performed using a DLS-8000DL (Otsuka electronics). The photo-stability was estimated from the photo-degradation curve as the relative emission intensity (I/I_0) with respect to the initial emission intensity (I_0) by using multichannel spectrometer (PMA-12, Hamamatsu Photonics) under 300–400 nm light (5 mW cm^{-2}) irradiation using a xenon light (MAX-303, Asahi Spectra) with a UV light intensity feedback control unit. UV light intensity was measured using a UV power meter (C9536-02/H9958-02, Hamamatsu Photonics). The photo-degradation test was measured by 200 times diluted solution as prepared glassy O-dots with 1 cm square optical quartz cell. Q-dots and neat O-dots were measured by using a solution having similar emission intensity to glassy O-dots sample solution.

2. Materials

The emitter **4CzIPN** was synthesized according to our published papers.[1] The hosts mCP and mCBP were purchased from Tokyo Chemical Industry (Tokyo, Japan). DSPE-PEG2k was purchased from Nacalai Tesque (Tokyo, Japan). Q-dots (λ_{em} = 450 nm, PEG coated) were purchased from Sigma-Aldrich (St. Louis, MO, USA). HEK293 cells were obtained from the European Collection of Authenticated Cell Cultures (ECACC). E-MEM, PBS(−), 0.05 w/v% trypsin 0.53 mmol L^{-1} ethylenediaminetetraaceticacid tetrasodiumsalt (EDTA·4Na) solution, penicillin-streptomycin solution, 200 mmol L^{-1} L-glutamine solution, and 0.4 w/v% tripan blue solution were purchased from Fuji Film-Wako Chemical (Tokyo, Japan). Fetal bovine serum (FBS) was purchased from Thermo Fisher Scientific, Inc. (Waltham, MA, USA).

4. Cell culturing and uptake

The HEK293 cells were grown in E-MEM with 10% FBS, 1% penicillin-streptomycin, and 1% *L*-glutamine at 37 °C in an incubator containing 5% CO_2. For imaging, cells (1.0×10^5 mL^{-1}) were placed on a 35 mm diameter glass-bottomed culture dish and allowed to adhere for 24 h before uptake of glassy O-dots. The glassy O-dots were added to the cell cultured dish (the final concentration of glassy O-dots is 0.2 mg mL^{-1}). After incubation at 37 °C and 5% CO_2 for 24 h, the original medium in the dish was removed completely. Subsequently, cells were washed three time by 180 μL of PBS(−). Then the cells were observed with a phase contrast and fluorescence microscope (Olympus, CKX53). The long-term O-dots tracing was performed with the previously described general cell culturing conditions. The cell viability was estimated using the following method with a Neubauer improved cell counter plate. The medium was completely removed from the cell culturing dish, and the cells were washed two times with PBS(−). The cells were then treated with trypsin-EDTA·4Na solution for 1 min at 37 °C. After adding of medium containing FBS to inactivate the trypsin, a tripan blue solution was added to the homogeneous cell solution. The cell viability was estimated by the ratio of living cells versus total cell numbers.

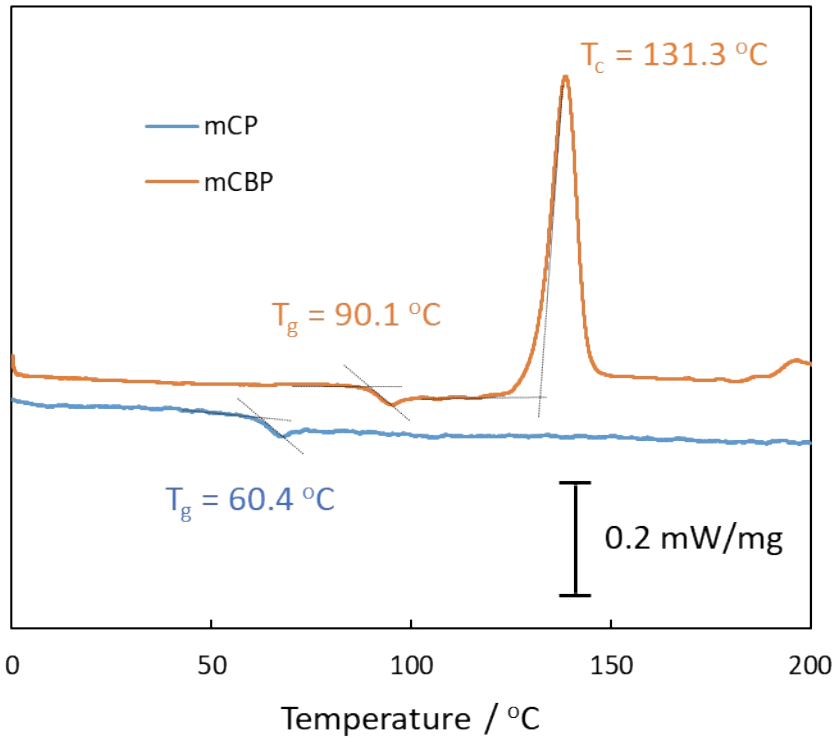

Fig. S1. Differential scanning calorimetry (DSC) characteristics of **mCP** and **mCBP**.

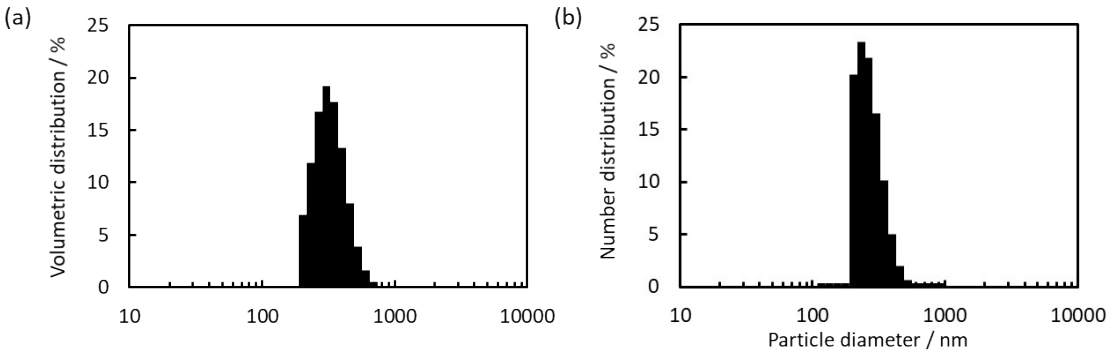

Fig S2. Size distribution diagrams of 6 wt% **4CzIPN** glassy O-dots; **mCP**:**DSPE-PEG2k** = 1.0

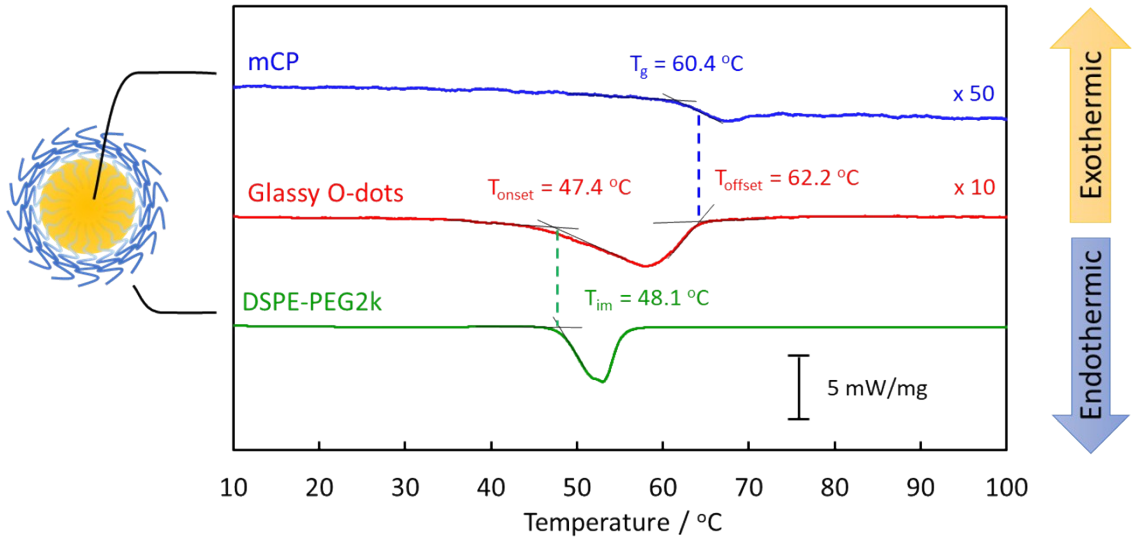

Fig. S3. Differential scanning calorimetry (DSC) characteristics of **mCP**, **DSPE-PEG-2k**, and glassy O-dots; **mCP**:**DSPE-PEG2k** = 10.

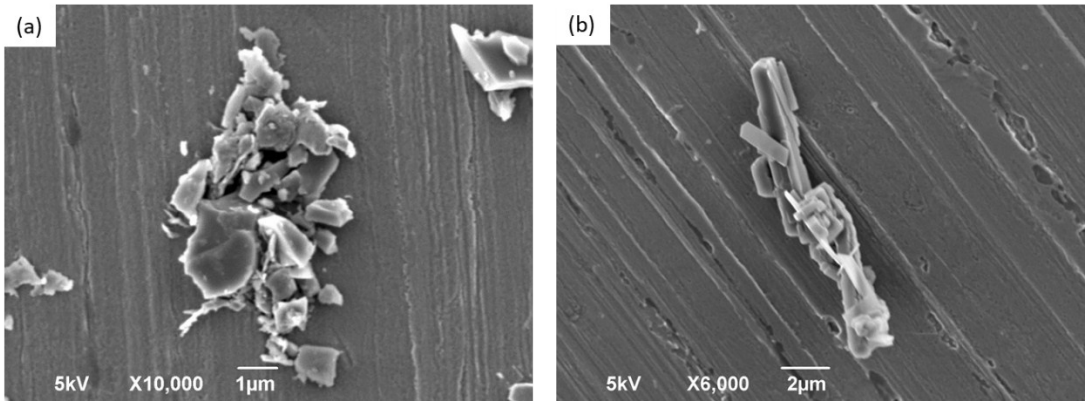

Fig S4. SEM images of the structures formed using the same fabrication conditions as for the glassy O-dots but with an emitter/guest combination of 6 wt% **4CzIPN**/**mCBP**; **mCP**:**DSPE-PEG2k** = 1.0.

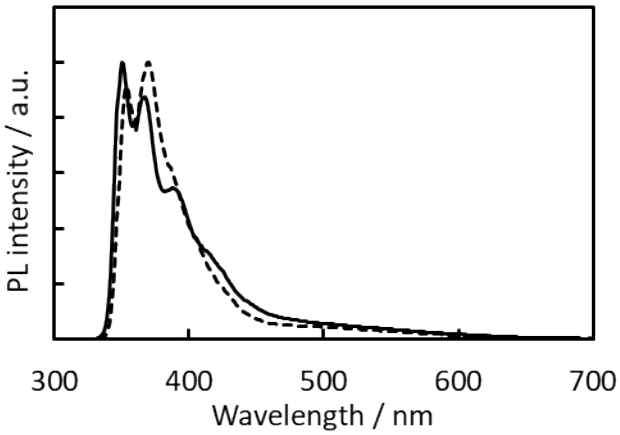

Fig. S5. Emission spectra of thermally evaporated **mCP** (solid line) and **mCBP** film (bloken line); excitation light wavelength, 280 nm.

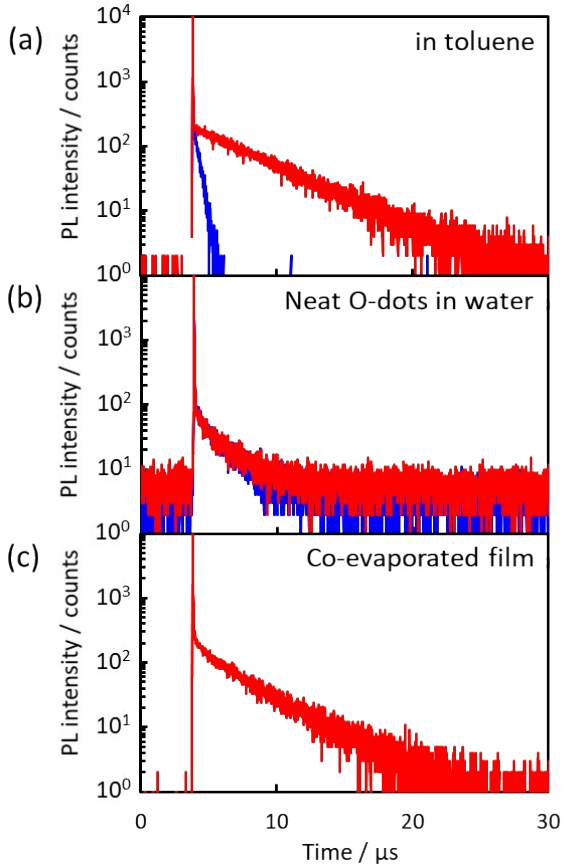

Fig. S6. Transient emission decay curves of **4CzIPN** in toluene at 500 nm (a), neat **4CzIPN** O-dots at 545 nm (b) and 6 wt% **4CzIPN** doped thermally evaporated **mCP** film at 515 nm (c); excitation light wavelength, 340 nm.

Table S1. PLQY and emission lifetime of **4CzIPN** in solution, O-dots and film states.

	mCP/DSPE-PEG2k ratio	λ_{max} (nm)	$\Phi_{w/o\ oxygen}$	Φ_{Air}	τ_{prompt} (ns)	τ_{delay} (μs)
in toluene*	—	498	0.83	0.24	16.2	4.7
4CzIPN neat O-dots	—	545	0.15	0.12	13.6	1.9
6 wt% 4CzIPN glassy O-dots processed in air saturated condition	10	516	0.64	0.64	18.0	3.1
6 wt% 4CzIPN glassy O-dots processed in oxygen free condition	1	516	0.94	0.93	16.6	3.1
6 wt% 4CzIPN glassy O-dots processed in oxygen free condition	10	516	0.91	0.90	16.6	3.0
6 wt% 4CzIPN mCP film	—	508	0.94	—	16.6	3.4
4CzIPN neat film	—	552	0.54	—	24.2	1.6

* 1.0×10^{-5} mol cm^{-3}

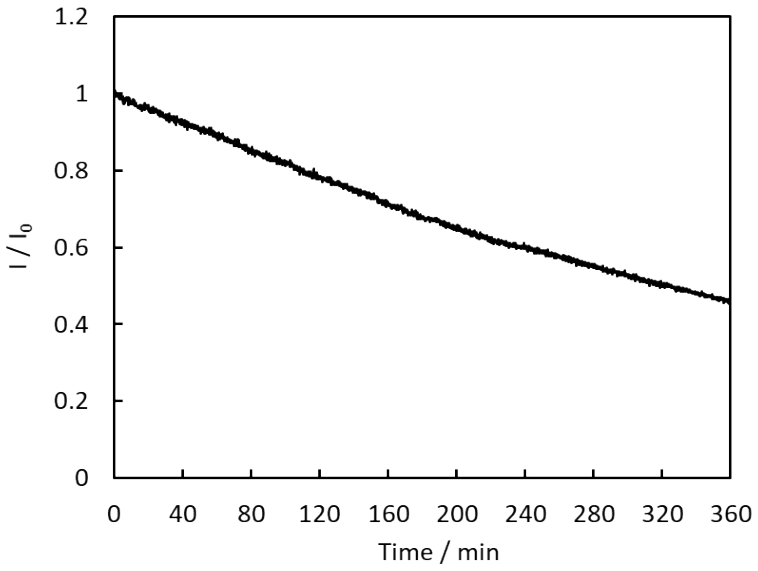

Fig. S7. Photo-degradation properties of 6 wt% **4CzIPN** glassy O-dots prepared in oxygen-free conditions in water (air saturated); observed wavelength, 515 nm; excitation light wavelength, 300–400 nm; excitation light intensity, 5 mW cm^{-2}; **mCP**:**DSPE-PEG2k** = 10:1.

Table S2. PLQY and lethal time to 75% (LT_{75}) and 50% (LT_{50}) photo-degradation for Q-dots, neat **4CzIPN** O-dots and 6 wt% **4CzIPN** glassy O-dots; excitation light wavelength, 300–400 nm; excitation light intensity, 5 mW cm^{-2}.

	Blue Q-dot	Neat O-dots	Glassy O-dots						
mCP/DSPE-PEG2k ratio	—	—	0.1	1	10	20	100	1	10
Φ_{PL}	≥ 50	0.12	0.50	0.64	0.64	0.62	0.63	0.94	0.91
LT_{75} (min)	60	1.5	1.5	9.4	23	43	45	115	140
LT_{50} (min)	140*	8.2	4.7	29	70	130*	130*	330*	360

* Estimation value from degradation curve

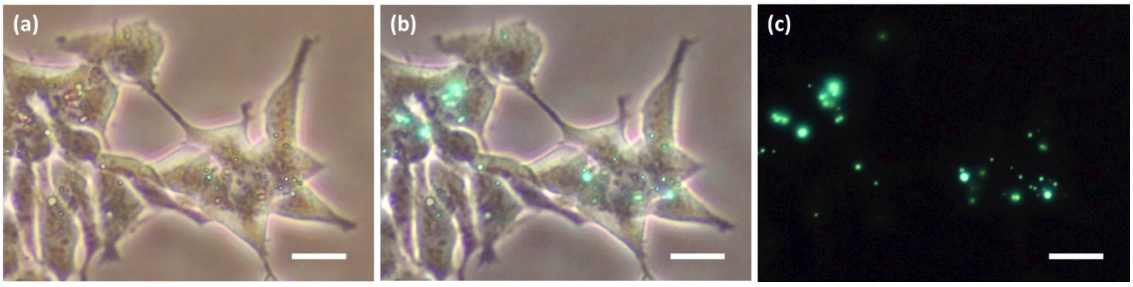

Fig. S8. Microscopic images of glassy O-dots (H/S ratio = 1.0) in HEK293 cells; after 3 passages over 7 days following uptake; (a) phase contrast image, (b) simultaneous observation images of phase contrast and fluorescence image and (c) fluorescence image; scale bar, 20 µm.

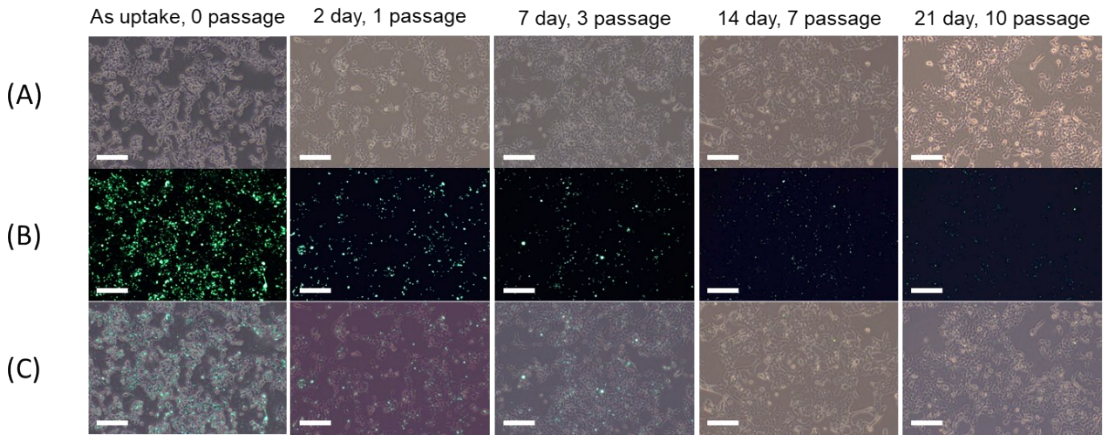

Fig. S9. Long term tracking microscopic images of glassy O-dots (**mCP**:**DSPE-PEG2k** = 1.0) in HEK293 cells; (a) phase contrast image, (b) fluorescence image and (c) simultaneous observation images, scale bar, 100 µm.

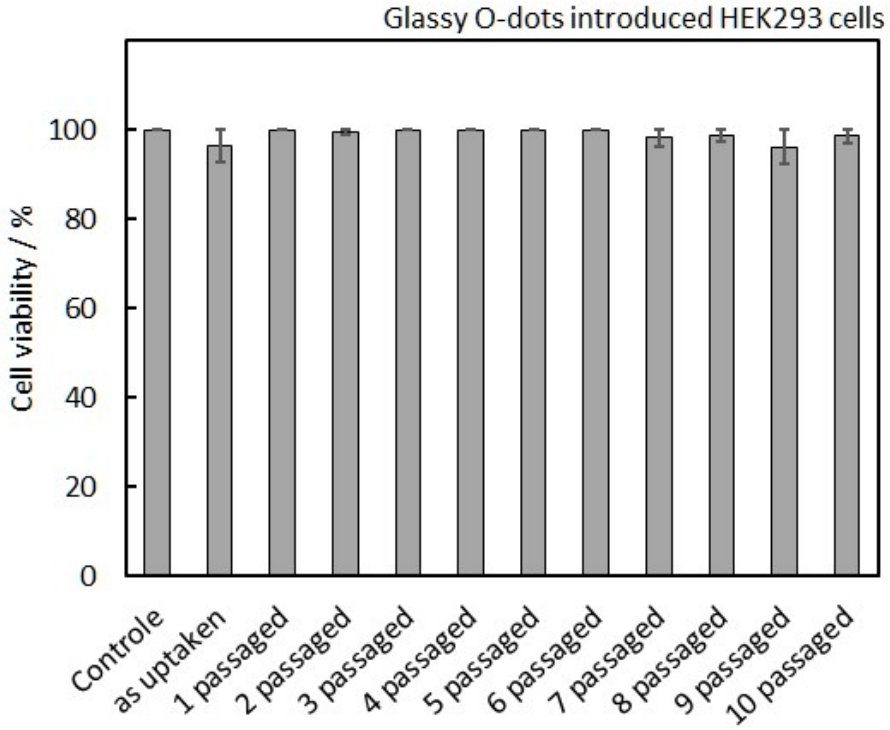

Fig. S10. Cell viability for HEK293 cells for uptake glassy O-dots (**mCP**:**DSPE-PEG2k** = 1.0) and during the culturing. The cell viability was estimated by the average for four measurements with tripan blue method.

References

1 H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, **492**, 234–238.