

Electronic Supplementary Information

Efficient green thermally activated delayed fluorescence (TADF) from a phenoxazine-triphenyltriazine (PXZ-TRZ) derivative

Hiroyuki Tanaka,^a Katsuyuki Shizu,^a Hiroshi Miyazaki,^{a,b}
and Chihaya Adachi^a

^aCenter for Organic Photonics and Electronics Research (OPERA), Kyushu University,
Motoooka 744, Nishi, Fukuoka 819-0395, Japan

^bFunctional Materials Laboratories, Nippon Steel Chemical Co., Ltd., 46-80 Nakabaru,
Sakinohama, Tobata, Kitakyushu, Fukuoka 804-8503, Japan

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SI-1. General Methods

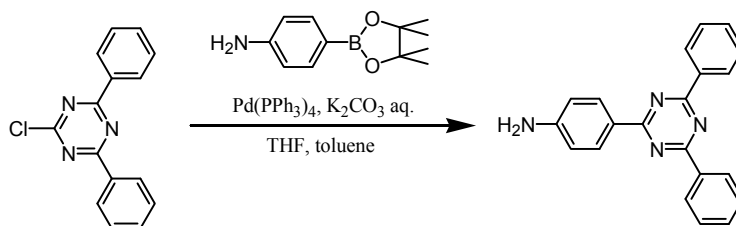
General. ^1H and ^{13}C NMR spectra were recorded on an Avance III 500 spectrometer (Bruker Biospin, Germany). MALDI-TOF mass spectra were obtained on an Autoflex III spectrometer (Bruker Daltonics, Germany) in reflection/positive mode with dithranol as a matrix. Solvents and starting materials were purchased from Tokyo Chemical Industry (Japan) or Wako Chemicals (Japan).

X-ray Crystallography. X-ray structure analyses were performed at Evaluation Center of Materials Properties and Function, Institute for Materials Chemistry and Engineering, Kyushu University. A single-crystal suitable for X-ray analysis was mounted on a glass fiber. The measurements were carried out at 124 K using a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo-K α radiation.

Photophysical measurements. Absorption spectra were measured with an Q. Photoluminescence spectra were measured with a photoluminescence spectrometer (Horiba Jovan Yvon, FluoroMax-4). PL quantum efficiency was measured with an absolute photoluminescence quantum yield measurement system (Hamamatsu, C9920-02, Japan). PL quantum yield and lifetime at a range of temperatures were measured with a streak camera system (Hamamatsu, C4334, Japan) equipped with a cryostat (IWATANI, GASESCRT-006-2000, Japan). A nitrogen gas laser (LASERTECHNIK BERLIN, MNL200) with an excitation wavelength of 337nm was used.

OLED fabrication and measurement. The PXZ-TRZ: CBP (15 nm) co-deposited films were fabricated by thermal deposition. The film thickness was monitored in-situ by an oscillating quartz thickness monitor during thermal deposition process. The current density-voltage-luminance (J-V-L) characteristics were measured at ambient temperature using a semiconductor parameter analyzer (Agilent, E5273A, USA).

SI-2. Synthetic routes of PXZ-TRZ

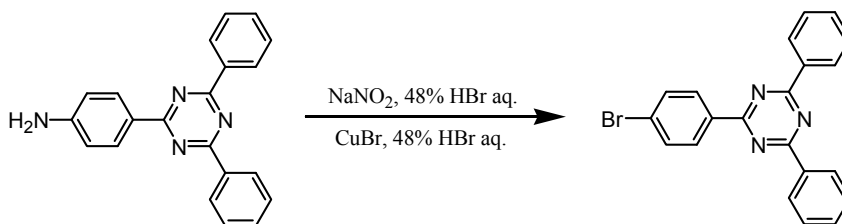


To a solution of 5.35 g of 2-Chloro-4,6-diphenyl-1,3,5-triazine (20 mmol), 4.82 g of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (22 mmol) and 1.16 g of Tetrakis(triphenylphosphine)palladium(0) (1.0 mmol) in 100 ml of THF were added dropwise, with stirring, a solution of 5.53 g of potassium carbonate (40 mmol) in 100 ml of water. Subsequently, the mixture was stirred and refluxed for 2 days. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Mg₂SO₄, and concentrated in vacuo. Then 100 ml of chloroform was added to it, the brown precipitate formed was collected by filtration, washed with 100 ml of chloroform, dried under vacuum, and 4.60 g of 2-Amino-4,6-diphenyl-1,3,5-triazine was obtained. The yield is over 71%.

[NMR]

¹H-NMR (CDCl₃, 300MHz) δ = 4.11(s, 2H), 6.80(d, 2H), 7.54-7.60(m, 6H), 8.61(s, 2H), 8.74(d, 4H)

[MS] MALDI-MS m/z: 324



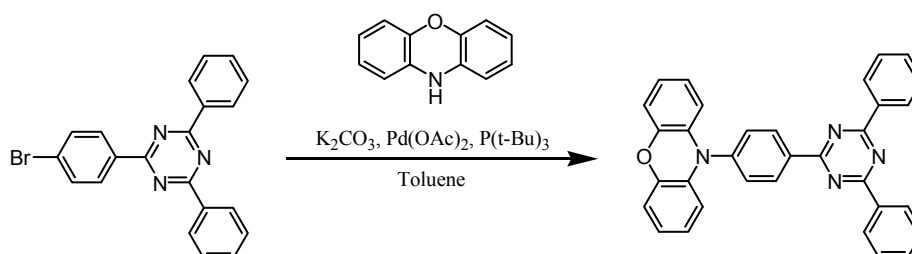
A mixture of 4.45 g of 2-Amino-4,6-diphenyl-1,3,5-triazine (13.7 mmol) and 20 ml of hydrobromic acid (47%) was cooled at 0-5°C by ice-bath. A cooled solution of 946.8 mg of NaNO₂ in 20 ml of water was added dropwise to the above solution. The mixture was stirred in ice-bath for one hour, a mixture of 1.18 g of copper bromide(I) (8.24mmol) and 8 ml of hydrobromic acid was added dropwise and stirred at RT for few minutes. The resulting mixture was stirred and refluxed overnight. Subsequently, the mixture was cooled by ice-bath and

neutralized with sodium hydrogen carbonate. Then 100 ml of chloroform was added to it, the organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over Mg_2SO_4 , and concentrated in vacuo. Column chromatography of the residue solid (eluent: chloroform/hexane=1/4) afforded 3.19 g of 2-Bromo-4,6-diphenyl-1,3,5-triazine. The yield is over 60%.

[NMR]

1H -NMR ($CDCl_3$, 300MHz) δ = 7.58(m, 6H), 7.70(d, 2H), 8.64(s, 2H), 8.76(s, 4H)

[MS] MALDI-MS m/z: 388



To a solution of 1.17 g of 2-Bromo-4,6-diphenyl-1,3,5-triazine (3.0 mmol), 611.2 mg of phenoxazine (3.3 mmol) and 1.24 g of potassium carbonate (9.0 mmol) in 30 ml of toluene was added, with stirring, a solution of 20.2 mg of palladium(II) acetate (0.09 mmol) and 66.8 mg of tri-tert-butylphosphine (0.33 mmol) in 30 ml of toluene. Subsequently, the mixture was stirred and refluxed for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over Mg_2SO_4 , and concentrated in vacuo. Column chromatography of the residue solid (eluent: chloroform/hexane=1/4) afforded 912.4 mg of PXZ-TRZ. The yield is over 62%.

[NMR]

1H -NMR ($CDCl_3$, 300MHz) δ = 6.04(d, 2H), 6.60(t, 2H), 6.66(t, 2H), 6.72(d, 2H), 7.57(m, 8H), 8.80(d, 4H), 8.99(d, 2H)

[MS] MALDI-MS m/z: 491

SI-3. Representative Crystal structure analysis of PXZ-TRZ

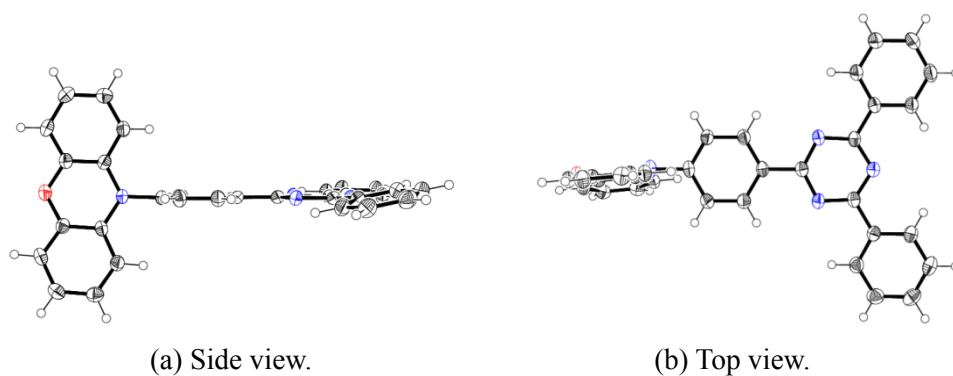


Fig. S1 ORTEP drawings for the asymmetric unit of PXZ-TRZ.

SI-4. Representative UV-vis absorption and PL spectra of PXZ-TRZ

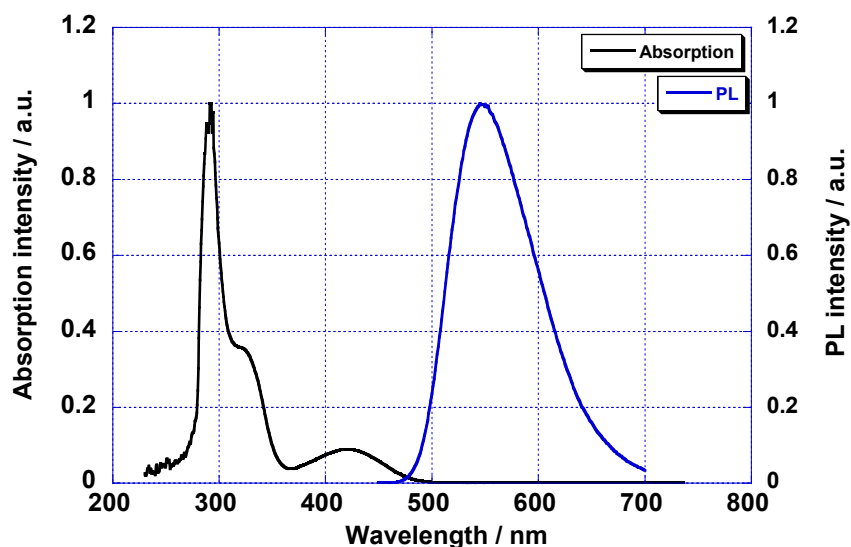


Fig. S2 UV-vis absorption (black) and PL (blue) spectra of PXZ-TRZ in toluene solution at the concentration of 10^{-5} mol/l. The PL spectrum was observed by exciting at 420 nm.

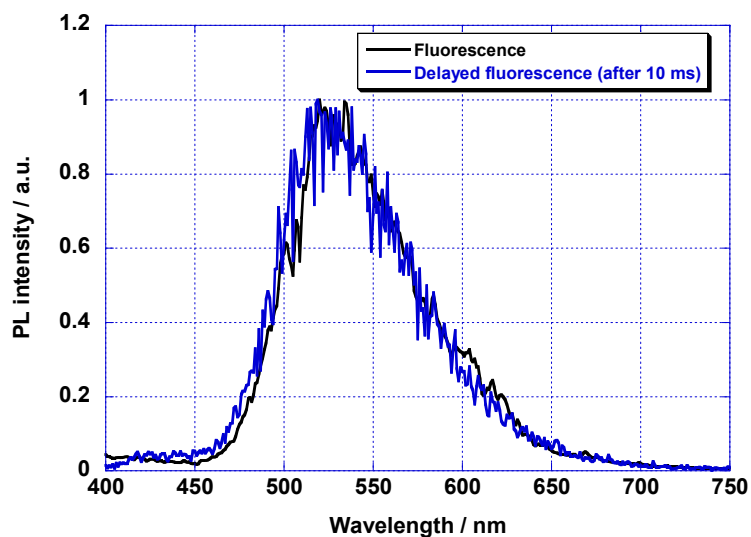
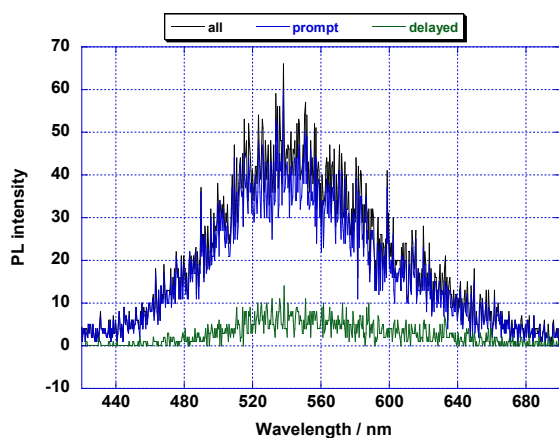
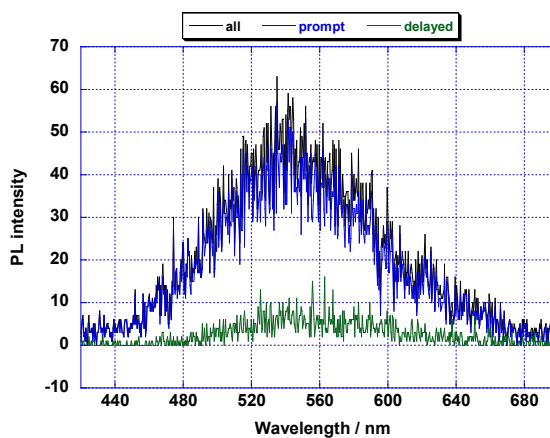


Fig. S3 Low temperature PL spectra (at 77 K) of PXZ-TRZ in 2-methylTHF solution at the concentration of 10^{-4} mol/l. Black and blue lines show prompt and delayed ($\tau > 9$ ms) spectra, respectively.

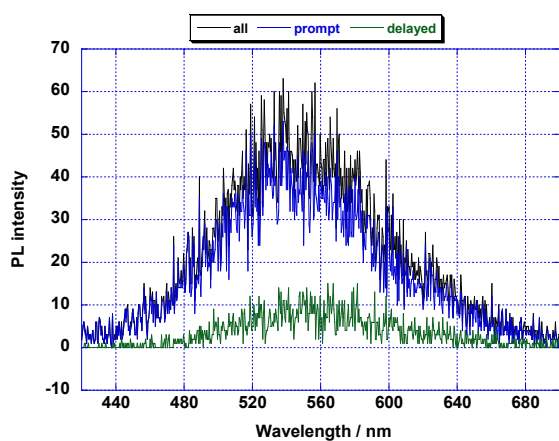
SI-5. Representative Temperature-dependence of PL spectrum of PXZ-TRZ



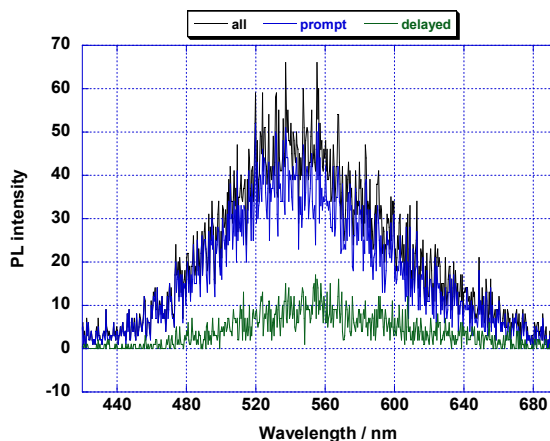
(a) 10 K



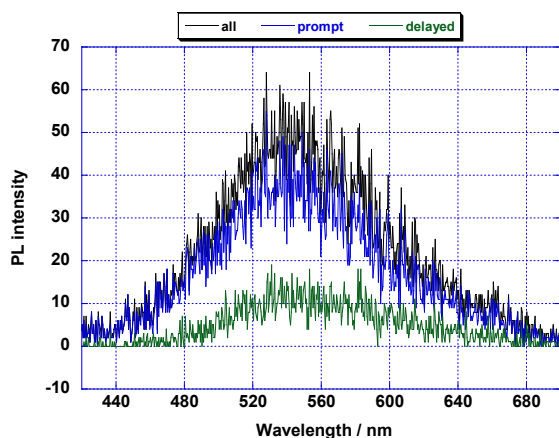
(b) 50 K



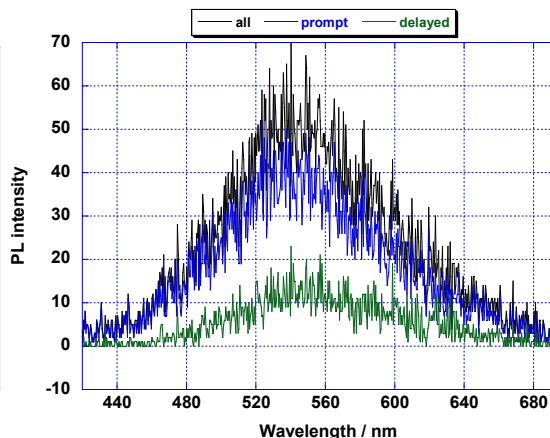
(c) 100 K



(d) 150 K



(e) 200 K



(f) 250 K

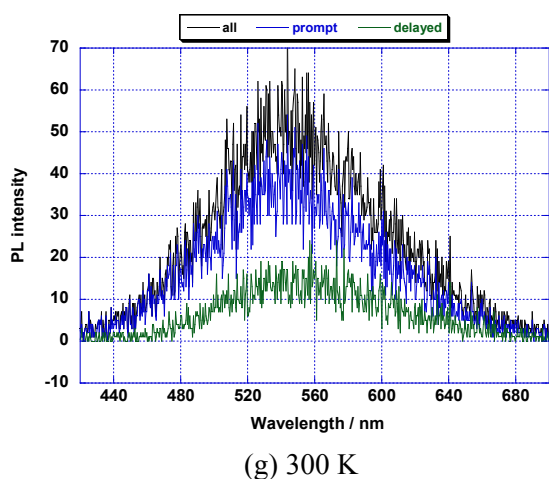


Fig. S4 Temperature dependence of PL spectra of a 6wt% doped film of PXZ-TRZ in a CBP host measured at (a) 10 K, (b) 50 K, (c) 100 K, (d) 150 K, (e) 200 K, (f) 250 K and (g) 300 K, respectively. Black, blue and green lines show integrated PL component, prompt component and delayed component, respectively.

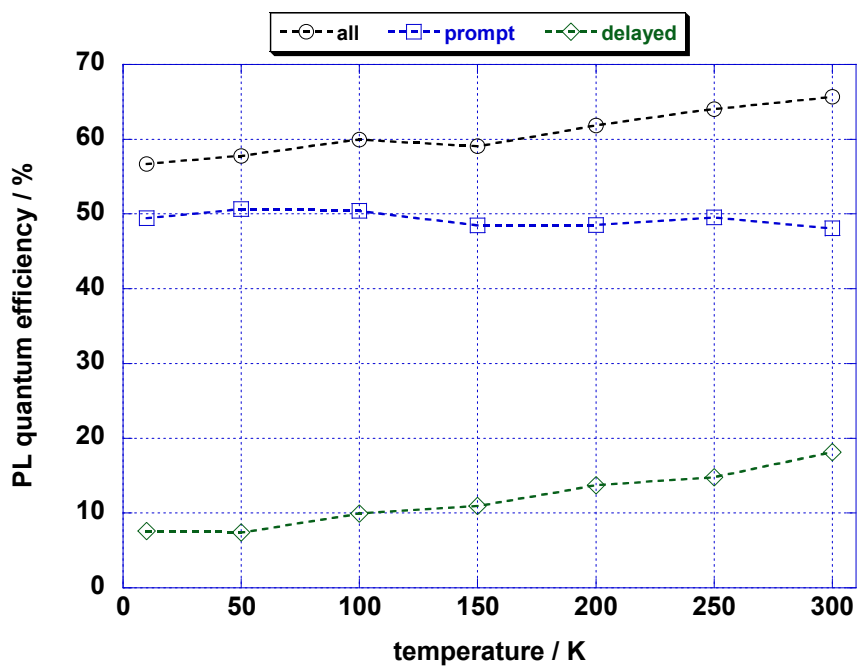


Fig. S5 Temperature dependence of PL quantum efficiency of (a) integrated PL intensity (black), (b) prompt component (blue) and (c) delayed component, respectively (green).

SI-6. Representative OLED characteristic (J - V - L) of PXZ-TRZ

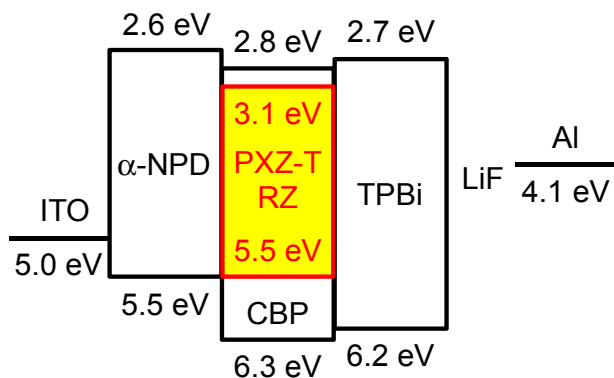


Fig. S6 Energy diagram for the OLED with the structure of ITO/ α -NPD/6wt% PXZ-TRZ:CBP/TPBi/LiF/Al.

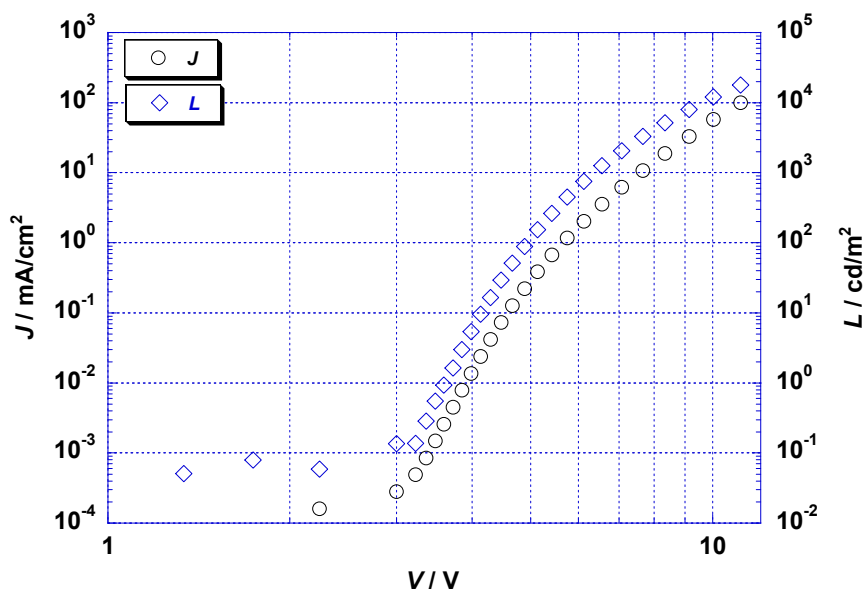


Fig. S7 Current density (J) vs. voltage (V) vs. luminance (L) plots of the OLED of ITO/ α -NPD/6wt% PXZ-TRZ:CBP/TPBi/LiF/Al. J - V plot and L - V plot are shown by circle and diamond, respectively.