Near-infrared organic light-emitting diode based on an Yb(III) complex

synthesized by vacuum co-deposition

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Methods

MALDI-TOF-MS were measured using a matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (AXIMA Confidensce, SHIMADZU) in the positive mode. Elemental analyses were carried out using a Yanaco MT-5 CHN corder. FT-IR spectra were measured using a Fourier-transform infrared spectrometer (FT/IR-6100, JASCO) with a reflection-absorption spectroscopy unit (RAS PRO410-H, JASCO). The absorption spectra were measured using a UV-Vis-NIR spectrophotometer (LAMBDA 950, Perkin Elmer). The photoluminescence spectra were measured using spectrofluorometers (FluoromMax, Horiba Jobin Yvon, and Quantaurus-QY Plus, Hamamatsu Photonics). The absolute photoluminescence quantum yields (Φ_{PL}) were measured using an integration sphere with an NIR photoluminescence measurement unit (Quantaurus-QY Plus, Hamamatsu Photonics). The NIR emission lifetime (τ_{obs}) was obtained using a NIR PMT unit (NIR-PMT module, H12397A-75-C2, Hamamatsu Photonics), and oscilloscope (MOS6104A, Agilent Technologies) excited by 337 nm N_2 pulse laser (KEN-X, USHO). The electroluminescence spectra of the OLEDs were measured using calibrated multichannel spectrometers (visible region: PMA12, Hamamatsu Photonics; NIR region: C9913GC, Hamamatsu Photonics). Currentdensity–voltage–luminance (*J-V-L*) characteristics were measured using a semiconductor parameter analyzer (E5273A, Agilent). Voltage-luminance (*V-L*) characteristics were measured using a calibrated photodetector (818-IG-L, Newport).

Calculation of sensitization efficiency and intrinsic quantum yield

The sensitization efficiency (η_{sens}) and the intrinsic quantum yield (ϕ_{Yb}) of Yb(DBM)$_3$(DPEPO) were calculated from equations (1) and (2) [1–3].

$$\phi_{\text{PL}} = \eta_{\text{sens}}\phi_{\text{Yb}} = \eta_{\text{sens}}\frac{\tau_{\text{obs}}}{\tau_{\text{rad}}} \tag{1}$$

$$\frac{1}{\tau_{\text{rad}}} = 2303 \times \frac{8\pi n^2 \tilde{v}^2 (2J+1)}{N_A(2J'+1)} \int \varepsilon(\tilde{v})\, d\tilde{v} \tag{2}$$

In these equations, η_{sens} is the sensitization efficiency parameter representing the efficiency of the ligand-to-metal energy transfer process, τ_{obs} is the observed luminescence lifetime, τ_{rad} is the natural radiative lifetime, n is the refractive index of the solvent, $\tilde{v}$ is the wavenumber of the transition in cm^{-1}, N_A is Avogadro's number, J and J' are the quantum numbers for the ground and excited states, and $\varepsilon(\tilde{v})$ is the molar absorption coefficient. We obtained values of $\eta_{\text{sens}} = 7.1\%$ and $\tau_{\text{rad}} = 751.4$ μs using $\tau_{\text{obs}} = 42.6$ μs from Fig. S1, $\phi_{\text{PL}} = 0.4\%$ measured with an integrating sphere and an InGaAs photodetector (excitation at 340 ± 20 nm), and $\varepsilon(\tilde{v})$ from Fig. S2.

Synthesis of Yb(DBM)$_3$(H$_2$O)$_2$[4]

   To a THF (40 mL) solution of HDBM (3.6 g, 16 mmol), trimethylamine (2.25 mL, 16.2 mmol) was added dropwise, and the mixture was stirred for 30 min. Then, Yb(CH$_3$COO)$_3$(H$_2$O)$_5$ (2.2 g, 5 mmol) in 20 mL of THF was added dropwise under stirring, and the solution was heated to reflux for 4 h. After cooling, toluene was added and THF was evaporated to afford a yellow powder. The resulting solution was filtered and a yellow powder was obtained. Then, the powder was dried overnight under vacuum and purified by sublimation (3.2 g, 3.6 mmol, 72%). MALDI-TOF-MS (dithranol) m/z = 844.29 ([M − 2H$_2$O + H]$^+$); IR (KBr) 1547, 1522 (st, C=O) cm^{-1}. Elemental analysis for C$_{45}$H$_{33}$O$_6$Yb, calculated C 64.13%, H 3.95%, found C 64.52%, H 3.85%.

Synthesis of Yb(DBM)₃(DPEPO)[1]

To a THF (20 mL) solution of $Yb(DBM)_3(H_2O)_2$ (1.39 g, 1.5 mmol), DPEPO (0.87 g, 1.5 mmol) was added under stirring, and the solution was heated to reflux for 2 h. After cooling, toluene was added, and then the solvent was evaporated to afford a yellow powder. The resulting solution was filtered, and the obtained yellow powder was then dried overnight under vacuum (1.7 g, 1.2 mmol, 83%). MALDI-TOF-MS (dithlanol) m/z = 1190.26 ([M − DBM]$^+$); IR (KBr) 1551, 1519 (st, C=O) cm^{-1}, 1121 (st, P=O) cm^{-1}; Elemental analysis for $C_{81}H_{61}O_9P_2Yb$, calculated C 68.83%, H 4.35%, found C 68.55%, H 4.46%.

Film and OLED fabrication

Organic films were thermal evaporated onto cleaned steel substrate for MALDI-TOF-MS, gold substrates for FT-IR-RAS, and quartz substrates for optical characterization under vacuum at pressures of $< 4 \times 10^{-4}$ Pa. The co-deposition rate was $Yb(DBM)_3(H_2O)_2$:DPEPO = 0.3 Å/s:0.2 Å/s (molar ratio = 1:1) and the thickness was 100 nm.

Glass substrates with a pre-patterned, 100-nm-thick, 100 Ohm sq^{-2} tin-doped indium oxide (ITO) coating were used as anodes. Substrates were washed by sequential ultrasonication in neutral detergent, deionized water, acetone, and isopropanol and then exposed to ultraviolet–ozone (NLUV253, Nippon Laser & Electronics Lab) to remove adsorbed organic species. After cleaning, the substrates were immediately transferred into the evaporation chamber.

Organic layers were formed by thermal evaporation. Doped emitting layers were deposited by co-evaporation. Deposition was performed under vacuum at pressures $< 4 \times 10^{-4}$ Pa. Devices were exposed to nitrogen gas once after formation of the organic layers to apply a metal mask that defines the cathode area.

OLEDs with the structure ITO/α-NPD (30 nm)/mCP (10 nm)/$Yb(DBM)_3(H_2O)_2$:DPEPO (30 nm)/DPEPO (10 nm)/TPBi (40 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated. The deposition rates of the $Yb(DBM)_3(H_2O)_2$:DPEPO layers were 0.3 Å/s:0.81 Å/s (molar ratio = 1:4), 0.3 Å/s:0.2 Å/s (molar ratio = 1:1), and 0.3 Å/s ($Yb(DBM)_3$ neat).
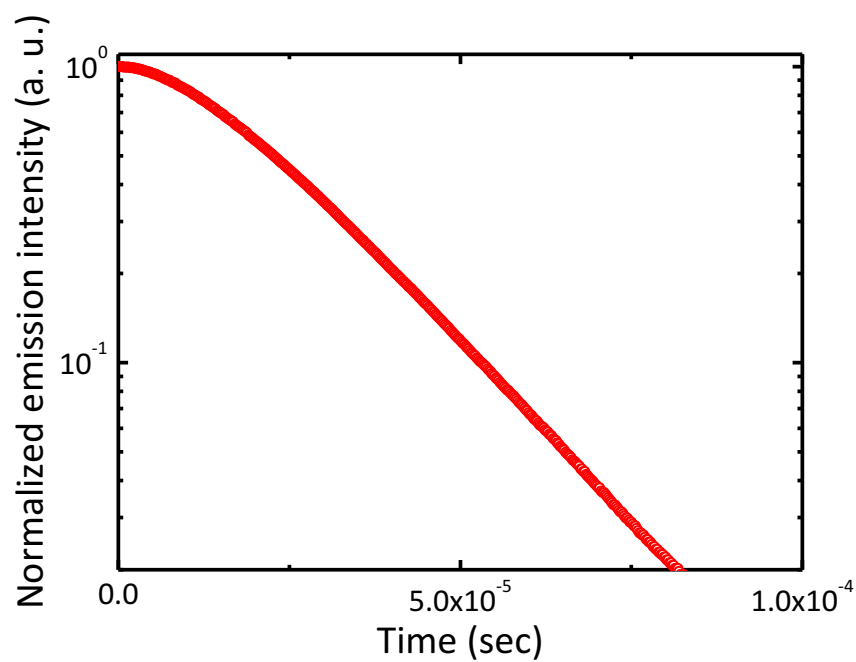
Fig. S1. NIR emission decay curve of Yb(DBM)$_3$(DPEPO) in DMSO solution (4.5×10^{-3} M, excited at 337 nm) measured using an NIR photomultiplier tube.
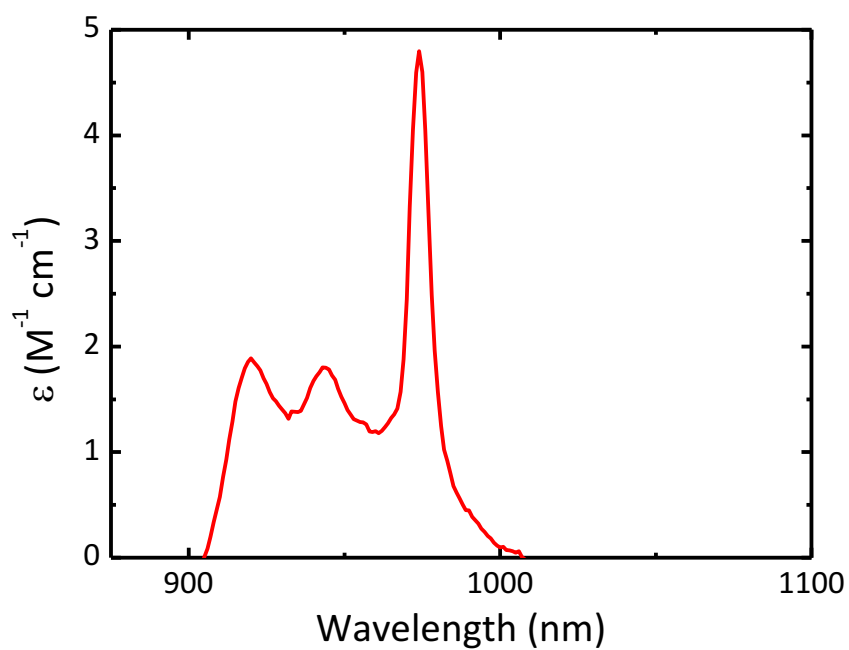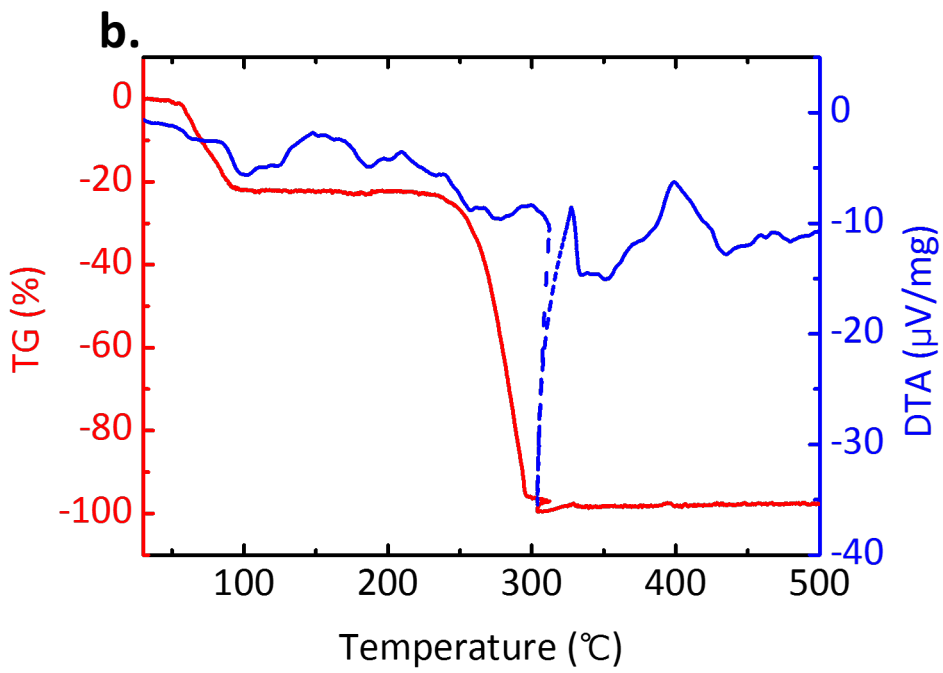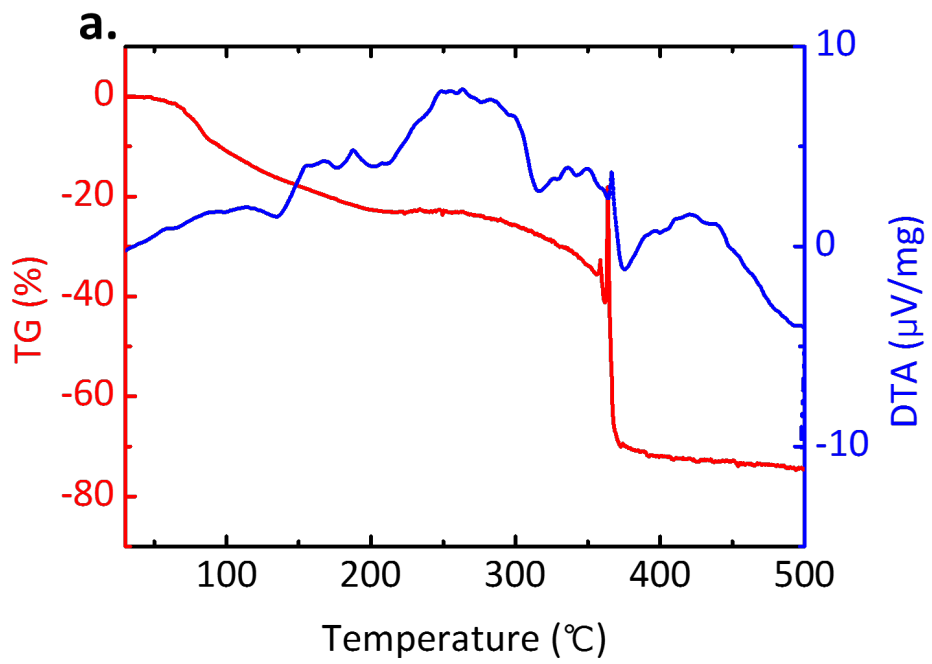

Fig S2. NIR absorption spectrum of Yb(DBM)$_3$(DPEPO) in DMSO solution (4.5×10^{-3} M).
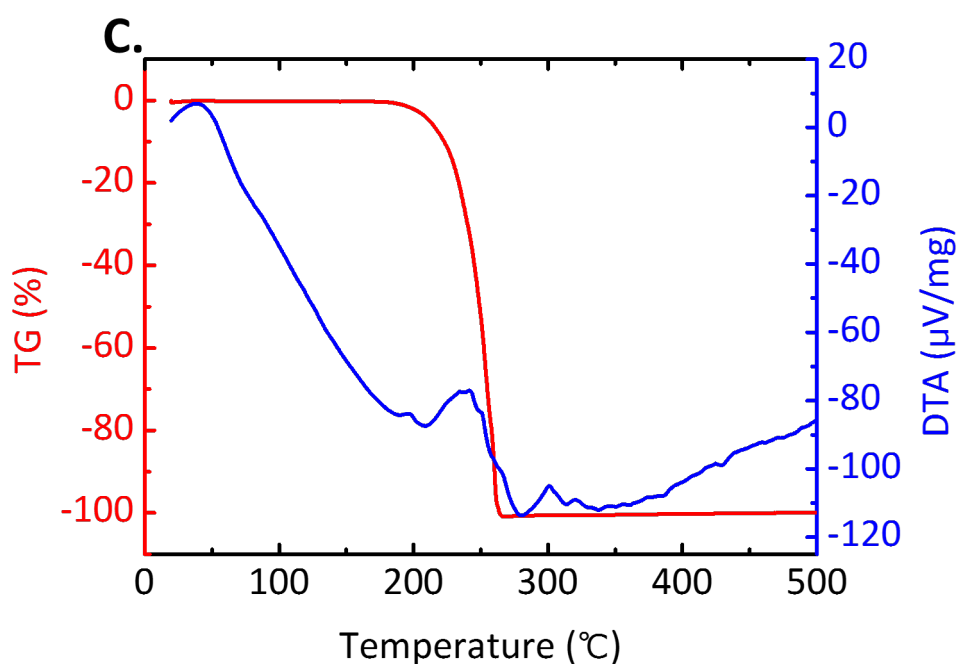
Fig. S3. (a) TG-DTA of Yb(DBM)$_3$(DPEPO), (b) Yb(DBM)$_3$(H$_2$O)$_2$ and (c) DPEPO under 1 Pa.
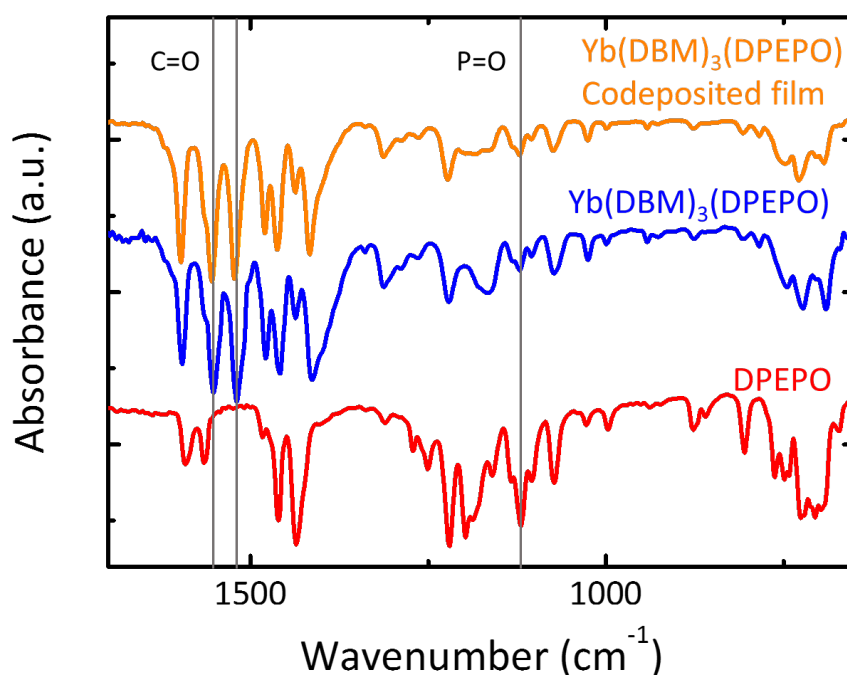
Fig. S4. FT-IR-RAS spectra of DPEPO (red), synthesized Yb(DBM)$_3$(H$_2$O)$_2$ (blue), deposited Yb(DBM)$_3$(H$_2$O)$_2$ film (green), synthesized Yb(DBM)$_3$(DPEPO) (orange), and co-deposited Yb(DBM)$_3$(DPEPO) film (purple).
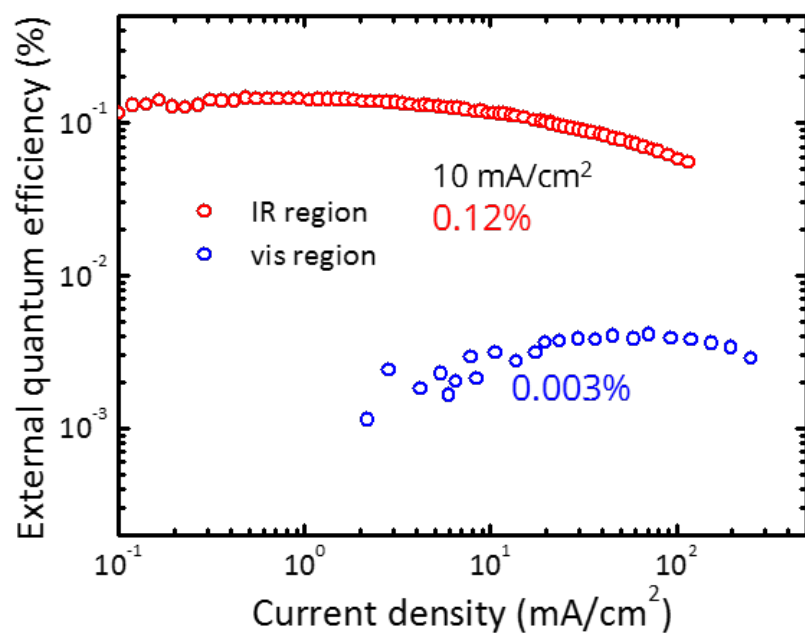
Fig. S5. Comparison of the η_{EQE}-J characteristics of device B in the IR and vis regions.
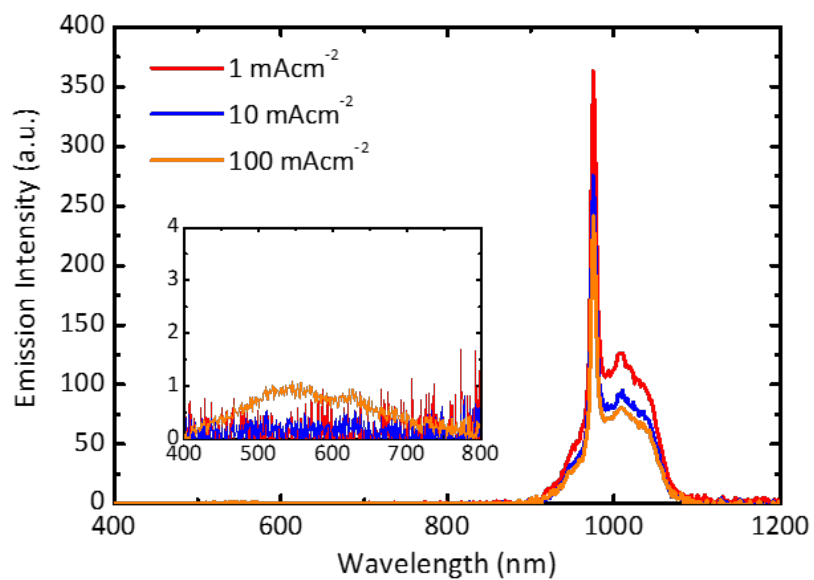

Fig. S6. The current density dependence of EL intensity of device B.

References

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