Electronic Supplementary Information (ESI)

Highly efficient exciplex organic light-emitting diodes incorporating a heptazine derivative as an electron acceptor

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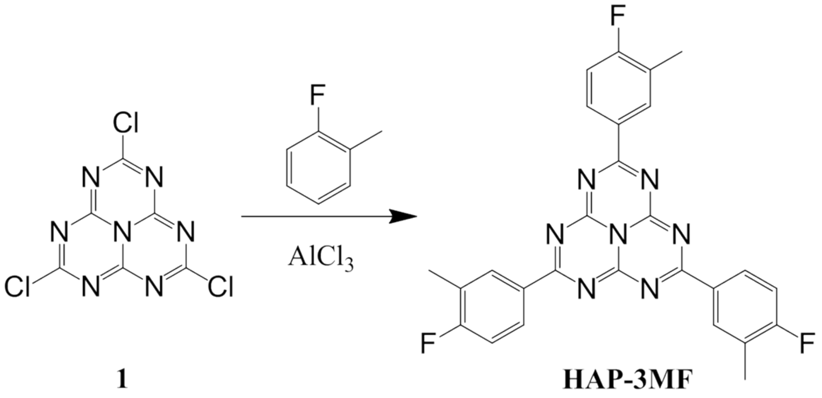
SI-1 General Methods

General. All spectrophotometric-grade solvents and starting materials were purchased and used as received unless otherwise noted. All reactions were carried out under N_2 atmosphere. ^{1}H NMR spectrum was obtained with a Bruker Biospin Avance-III 500 NMR spectrometer at ambient temperature. Because **HAP-3MF** was not sufficiently soluble in common deuterated solvents, its ^{13}C NMR spectrum was not obtained. High-resolution mass spectrometry (HRMS) by fast atom bombardment was conducted using a JEOL JMS-700 spectrometer. Elemental analysis was performed with a Yanaco MT-5 elemental analyzer.

Photophysical characterization. Organic films for optical measurements (100 nm) were deposited on quartz and silicon substrates by vacuum thermal evaporation at a pressure lower than 4×10^{-4} Pa. Absorption spectra were measured with a UV-vis spectrophotometer (UV-2550, Shimadzu), and PL spectra were recorded with a spectrofluorometer (FluoroMax-4, Horiba Jobin Yvon). The transient PL decay characteristics of film samples were measured with a streak camera (C4334, Hamamatsu Photonics) equipped with a cryostat (CRT-006-2000, Iwatani Industrial Gases) under air and vacuum conditions, and a nitrogen gas laser (MNL200, Lasertechnik Berlin) was used. PLQEs were measured using an integrating sphere (C9920–02, Hamamatsu Photonics) with a Xe lamp as the excitation source and a multichannel spectrometer (Hamamatsu PMA-11) as the optical detector. The highest occupied molecular orbital (HOMO) energy level of **HAP-3MF** was determined by atmospheric ultraviolet photoelectron spectroscopy (UPS) (AC-3E, Riken Keiki), and the lowest unoccupied molecular orbital (LUMO) level was calculated by subtracting the energy gap from the HOMO level.

OLED fabrication and measurements. The OLED devices were fabricated by vacuum thermal evaporation onto ITO-coated glass substrates. Prior to the vacuum thermal deposition of the organic layers, the ITO substrates were ultrasonically cleaned with detergent, deionized water, acetone, and isopropanol in sequence, and then treated with ultraviolet/ozone plasma for 15 min. The ITO substrate was then loaded into a vacuum chamber with a pressure lower than 4 $\times 10^{-4}$ Pa. A 30-nm-thick α-NPD layer was deposited on the substrates as a hole transport layer. Subsequently, a 10-nm-thick TCTA layer was evaporated to form an electron blocking layer, followed by a 20-nm-thick emission layer with a structure of 8/25/50/100 wt% **HAP-3MF**:**mCP**. A 10-nm-thick DPEPO layer was then deposited as a hole blocking layer, followed by a 40-nm-thick TPBI electron transport layer. Finally, the cathode layer was fabricated from 0.8-nm-thick LiF and 100-nm-thick Al layers. The intersection of ITO and the metal electrodes gave an active device area of 4 mm^2. The OLEDs were characterized in air without any encapsulation or light out-coupling enhancement. The *J-V-L* characteristics of OLEDs were measured using a semiconductor parameter analyzer (E5270, Agilent) with an optical power meter (1930C, Newport). EL spectra were obtained using a spectrometer (SD2000, Ocean Optics).

SI-2 Synthetic route to HAP-3MF



***2,5,8-Trichloro-1,3,4,6,7,9,9b-heptaazaphenalene* (1):** Compound **1** was synthesized according to the method reported previously.[1]

***2,5,8-tris(4-fluoro-3-methylphenyl)-1,3,4,6,7,9,9b-heptaazaphenalene* (HAP-3MF):** Compound **1** (1.0 g, 3.6 mmol) was added to a solution of $AlCl_3$ (2.41 g, 18 mmol) in 2-fluorotoluene (10 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then at 80 °C for 6 h. The reaction mixture was cooled to room temperature, ice was added, and the mixture was stirred for vigorously for 1 h. Subsequently, the mixture was heated at 100 °C for 30 min, allowed to cool to room temperature, filtered, washed with H_2O, and then taken up in toluene and pre-adsorbed onto silica. The pre-adsorbed materials were subjected to flash chromatography (EtOAc/toluene, 0:100 *v/v* and then 10:90 *v/v*) to give **HAP-3MF** (1.07 g, yield: 60%) as a yellow-green solid. **HAP-3MF** was further purified by sublimation. ^{1}H NMR (500 MHz, C_6D_6): δ 8.63 (dd, *J* =7.5, 1.5 Hz, 1H), 8.58–8.55 (m, 1H), 6.79 (t, *J* = 8.8 Hz, 1H), 2.05 (s, 3H). mp: 375–385 ^{o}C. HRMS (*m/z*): $[M]^-$ calcd for $C_{27}H_{18}N_7F_3$: 497.1576; found: 497.1558. Elemental anal. calcd for $C_{27}H_{18}N_7F_3$ (%): C 65.19, H 3.65, N 19.71; found: C 65.05, H 3.63, N 19.81.

References

1 J. Li, T. Nakagawa, J. MacDonald, Q. Zhang, H. Nomura, H. Miyazaki and C. Adachi, *Adv. Mater.*, 2013, **25,** 3319.

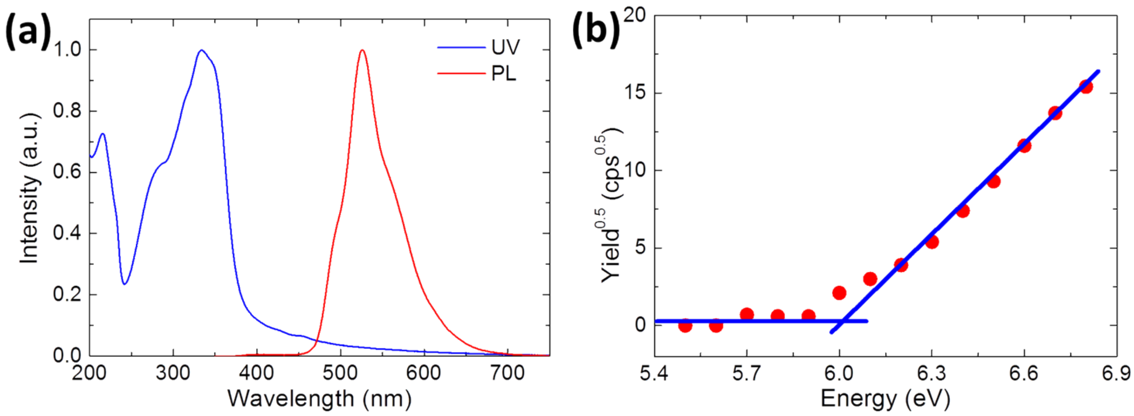


Fig. S1 (a) UV-vis absorption and PL spectra and (b) UPS of **HAP-3MF** in a solid film. The predominant absorption peak is centered at 334 nm, and the band gap was calculated to be 2.6 eV. The HOMO level of **HAP-3MF** was determined to be –6.0 eV by UPS. Therefore, the LUMO of **HAP-3MF** was calculated to be –3.4 eV by subtracting the band gap from the HOMO level.

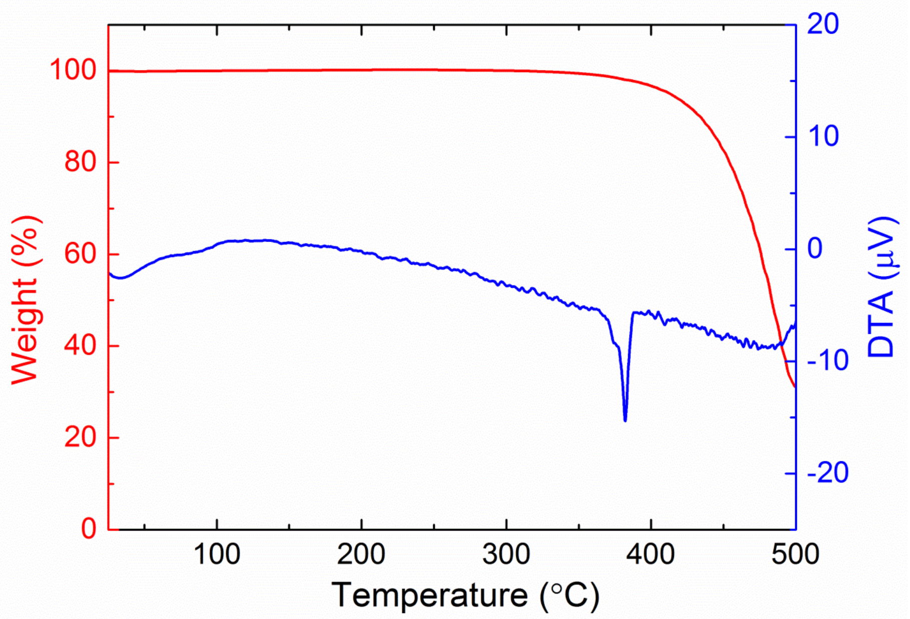


Fig. S2 TG-DTA of **HAP-3MF** under nitrogen flow. **HAP-3MF** is thermally stable up to around 370 °C. In addition, the initial decomposition temperature of **HAP-3MF** with a 5% weight loss is 413.5 °C.

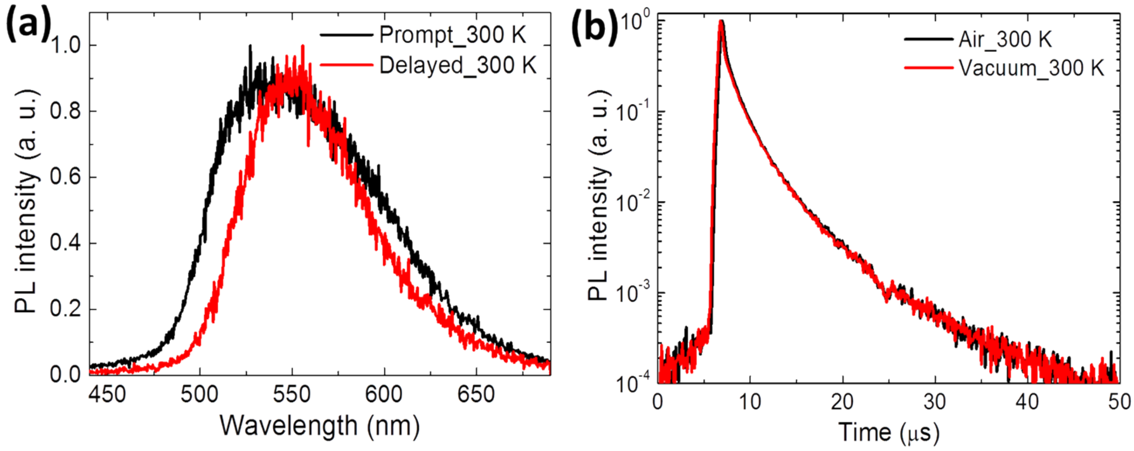


Fig. S3 Transient PL decay properties of a 25 wt% **HAP-3MF**:**mCP** exciplex system. (a) Prompt and delayed PL spectra under vacuum condition at 300 K. (b) Transient PL decay in air and under vacuum conditions at 300 K.

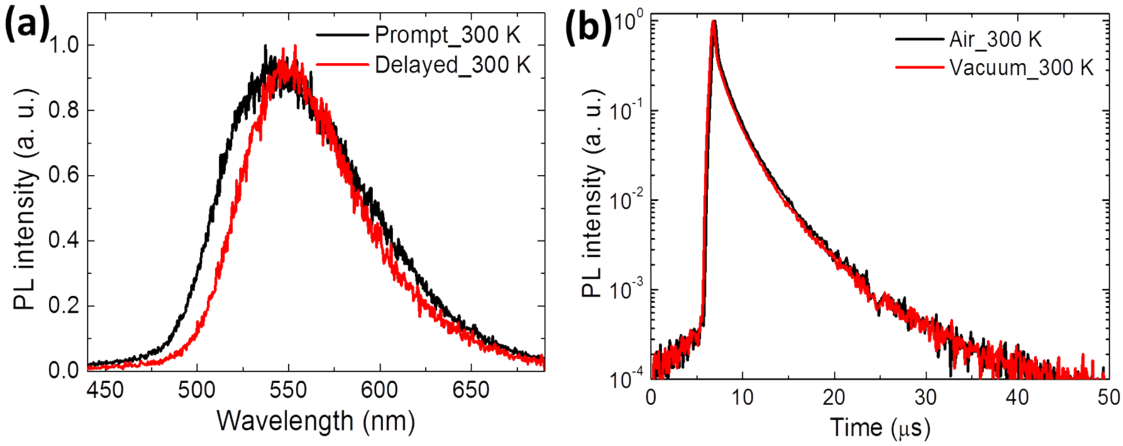


Fig. S4 Transient PL decay properties of a 50 wt% **HAP-3MF**:**mCP** exciplex system. (a) Prompt and delayed PL spectra under vacuum condition at 300 K. (b) Transient PL decay in air and under vacuum conditions at 300 K.

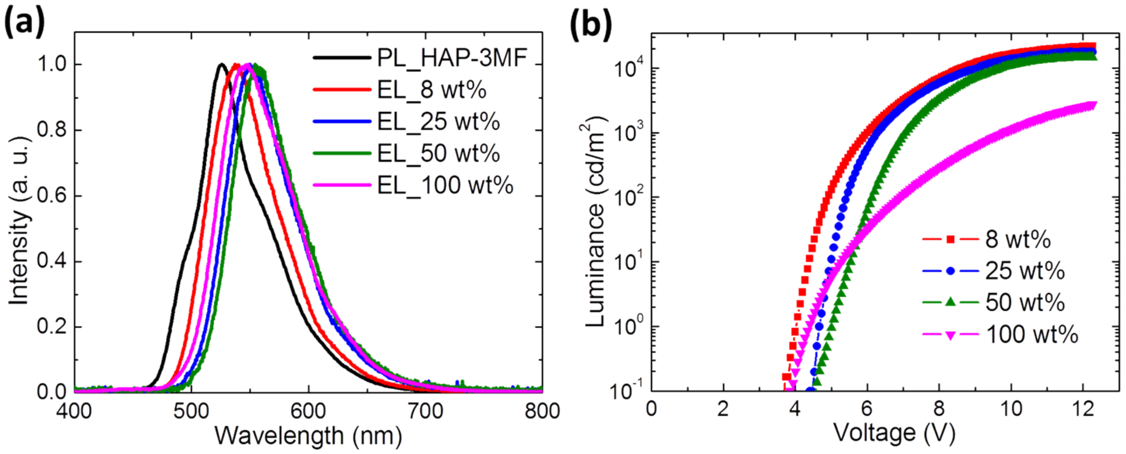
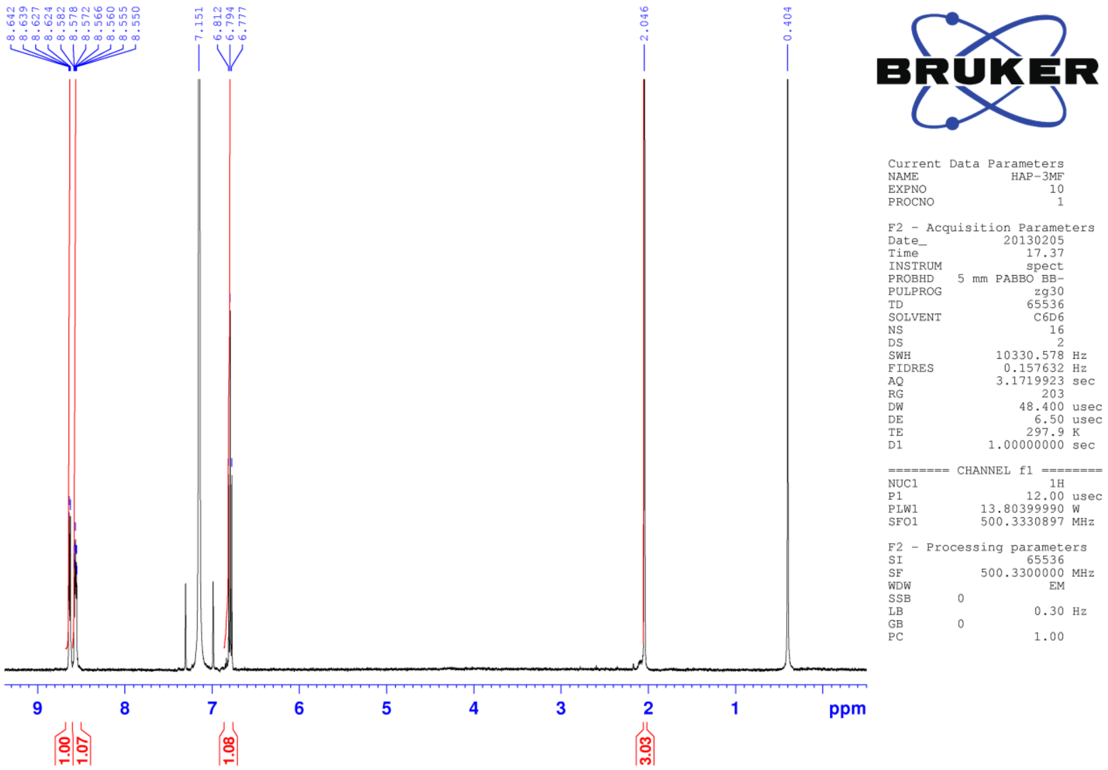


Fig. S5 EL performance of ExOLEDs containing **HAP-3MF**:**mCP** systems with various weight ratios. (a) EL spectra at a current density of 10 mA/cm^2. The EL spectra for 8 wt%, 25 wt% and 50 wt% **HAP-3MF**:**mCP** systems are centered at 538 nm, 550 nm and 555 nm, respectively, which are highly consistent with their PL spectra. While for the OLED incorporating 100 wt% **HAP-3MF**:**mCP** system as an emitting layer, it should be noted that its EL spectrum (centered at 548 nm) was red-shifted as compared to the PL spectrum of 100 wt% **HAP-3MF**:**mCP** film (centered at 526 nm). This should be due to exciplex formation at the interface between TCTA and **HAP-3MF** in view of the OLED structure. (b) Luminance as a function of voltage. The maximum luminance follows the EQE trends, with 22000 cd/m^2 in 8 wt%, 17589 cd/m^2 in 25 wt%, 14866 cd/m^2 in 50 wt% and 2714 cd/m^2 in 100 wt% **HAP-3MF**:**mCP** systems. Therefore, the maximum luminance decreased as the weight ratio of **HAP-3MF** was increased. We believe that concentration quenching plays a very important role in the EL process based on planar molecular geometry of **HAP-3MF** and OLEDs performance.



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PROCNO                   1

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PULPROG               zg30
TD                   65536
SOLVENT               C6D6
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719923 sec
RG                     203
DW                  48.400 usec
DE                    6.50 usec
TE                   297.9 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PLW1           13.80399990 W
SFO1           500.3330897 MHz

F2 - Processing parameters
SI                   65536
SF             500.3300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

Fig. S6 ^{1}H NMR spectrum of **HAP-3MF** in C_6D_6.

Table S1 PLQEs of **HAP-3MF**:**mCP** exciplex systems with various weight ratios in air and nitrogen.

	PLQE in air	PLQE in nitrogen
8 wt% **HAP-3MF**:**mCP**	0.658	0.661
25 wt% **HAP-3MF**:**mCP**	0.543	0.557
50 wt% **HAP-3MF**:**mCP**	0.440	0.470
100 wt% **HAP-3MF**:**mCP**	0.127	0.127