Supplementary Information

Delayed Fluorescence from Inverted Singlet and Triplet Excited States for Efficient Organic Light-Emitting Diodes

Naoya Aizawa[1,2]*, Yong-Jin Pu[1,3]*, Atsuko Nihonyanagi[1], Ryotaro Ibuka[1], Hiroyuki Inuzuka[1], Barun Dhara[1], Yuki Koyama[1,3], Fumito Araoka[1] and Daigo Miyajiam[1]*

[1] RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan.

[2] Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

[3] Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan.

Corresponding Authors: E-mail: naoya.aizawa@riken.jp; yongjin.pu@riken.jp; daigo.miyajima@riken.jp

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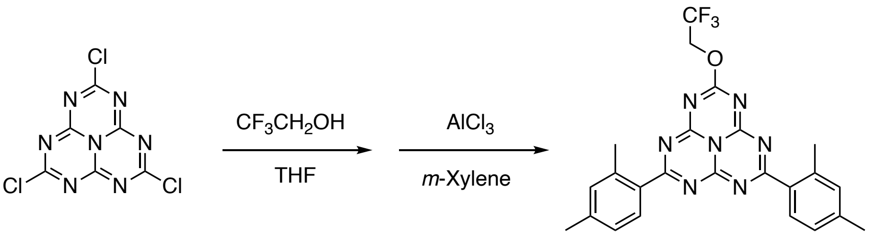
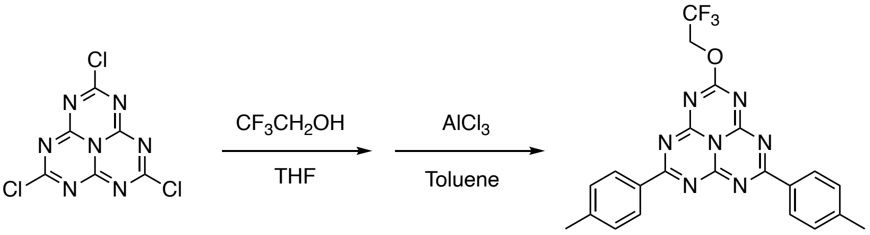


HzTFEX$_2$

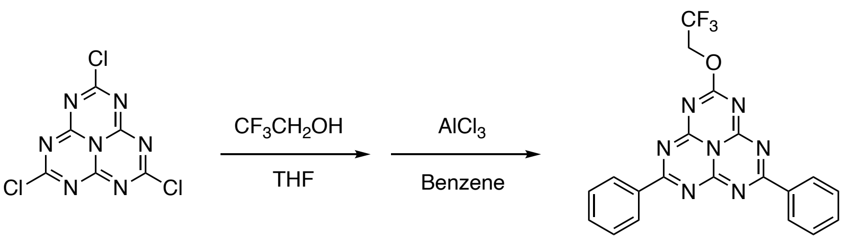
Synthesis of HzTFEX$_2$ 60% NaH oil dispersion (121 mg, 3.0 mmol) was added to a solution of 2,2,2-trifluoroethanol (199 μL, 2.78 mmol) in THF (10 mL) at 0 °C. After stirring for 30 min, the solution was added dropwise to a solution of 2,5,8-trichloroheptazine (700 mg, 2.53 mmol) in THF (20 mL) at 0 °C. After stirring for 2 h, the mixture was concentrated under reduced pressure to give a yellow solid. The crude products were used in the next step without further purification. The crude products were dissolved in *m*-xylene (12 mL), and $AlCl_3$ (1.0 g, 7.5 mmol) was added to the mixture at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then for 17 h at room temperature and quenched with H_2O. After the addition of $CHCl_3$ and stirring for 30 min, the organic phase was separated, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel ($CHCl_3$) to give 116 mg (0.242 mmol, 9.6%) of yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 2.39 (s, 6H), 2.73 (d, J = 4.8 Hz, 6H), 4.88 (q, J = 8.2 Hz, 2H), 7.11–7.13 (m, 4H), 8.19 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ [ppm] = 21.61, 23.15, 64.47, 126.91, 130.88, 132.49, 133.29, 141.57, 144.46, 157.28, 158.84, 170.12, 178.40. ^{19}F NMR (600 MHz, $CDCl_3$) δ [ppm] = –73.67 (s). MS (FD-TOF): 479.16915 $[M]^+$, calcd. for $C_{24}H_{20}F_3N_7O$ (479.16814), error = 2.1 ppm.



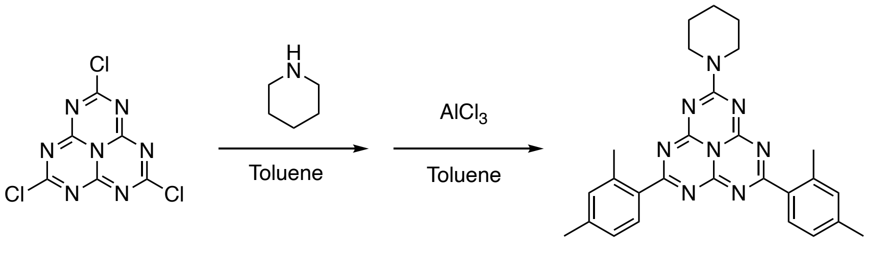
HzTFET$_2$

Synthesis of HzTFET$_2$ The synthetic procedure was the same as that of HzTFEX$_2$ except that toluene was used in place of *m*-xylene. ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 2.46 (s, 6H), 4.90 (q, J = 8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 4H), 8.45 (d, J = 8.4 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ [ppm] = 25.51, 67.89, 133.17, 134.11, 134.43, 150.23, 161.31, 162.48, 173.28, 178.90. ^{19}F NMR (600 MHz, $CDCl_3$) δ [ppm] = –74.12 (s). MS (FD-TOF): 451.13667 $[M]^+$, calcd. for $C_{22}H_{16}F_3N_7O$ (451.13684), error = 0.37 ppm.



HzTFEP$_2$

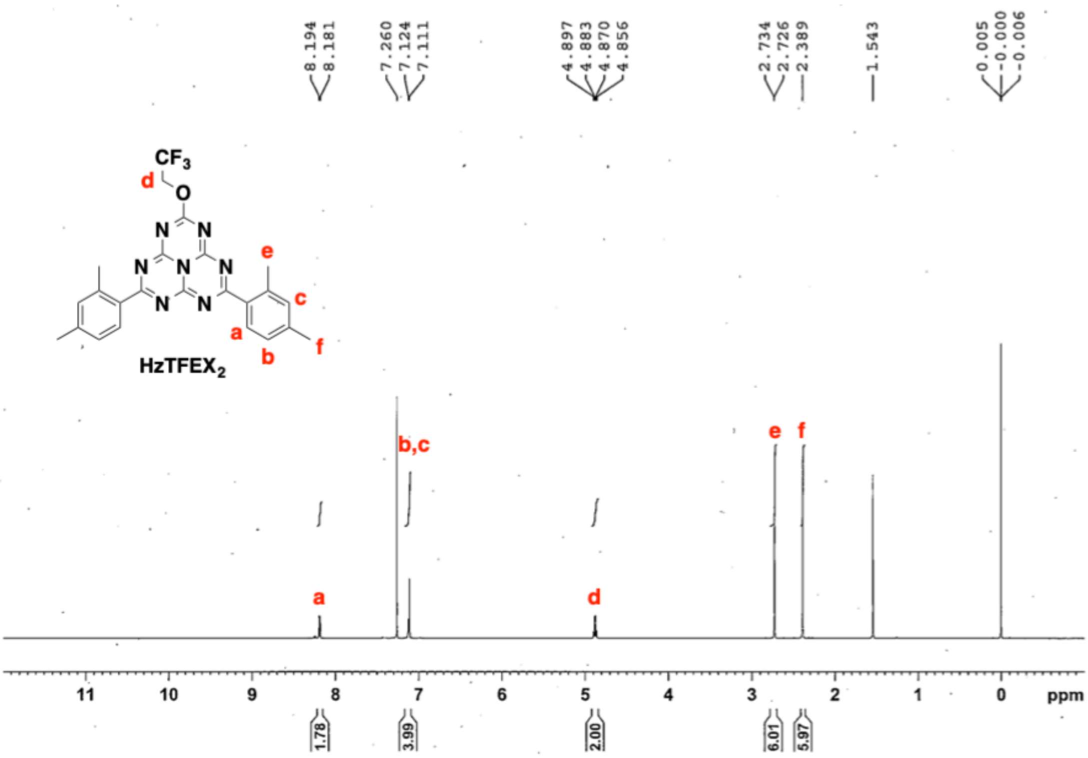
Synthesis of $HzTFEP_2$ The synthetic procedure was the same as that of $HzTFEX_2$ except that benzene was used in place of *m*-xylene. ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 4.92 (q, *J* = 8 Hz, 2H), 7.53 (dd, *J* = 7.8 Hz, 4H), 7.68 (dd, *J* = 7.2 Hz, 2H), 8.56 (d, *J* = 7.2 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ [ppm] = 64.60, 128.78, 130.70, 133.65, 135.07, 158.33, 159.45, 170.22, 176.03. ^{19}F NMR (600 MHz, $CDCl_3$) δ [ppm] = –73.69 (s). MS (FD-TOF): 423.10465 $[M]^+$, calcd. for $C_{20}H_{12}F_3N_7O$ (423.10554), error = 2.1 ppm.



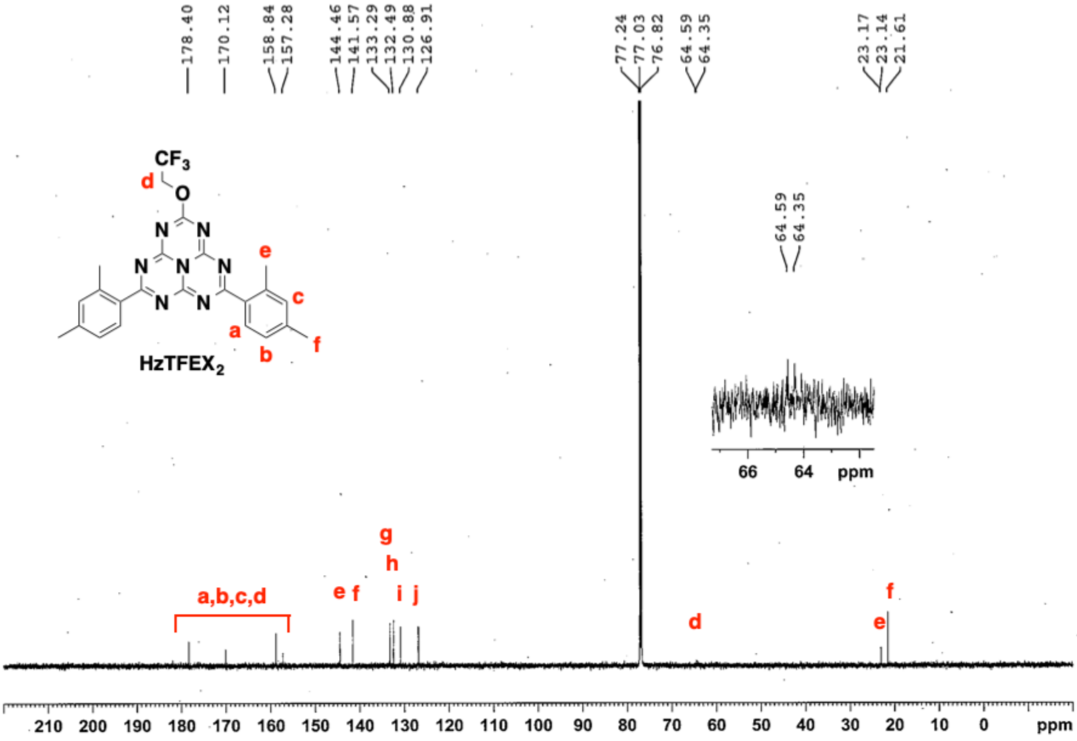
$HzPipX_2$

Synthesis of $HzPipX_2$ To a solution of 2,5,8-trichloroheptazine (100 mg, 0.362 mmol) in toluene (3 mL) was added piperidine (36 µL, 0.36 mmol) at room temperature. After 30 min of stirring at 100 °C, the mixture was allowed to cool to room temperature, and $AlCl_3$ (106 mg, 0.795 mmol) was added. The reaction mixture was stirred for 1 h at 100 °C and diluted with H_2O and $CHCl_3$ at room temperature. The organic phase was separated, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (AcOEt/$CHCl_3$ = 0:100 to 1:20) to give 19 mg (0.044 mmol, 12%) of yellow solid.

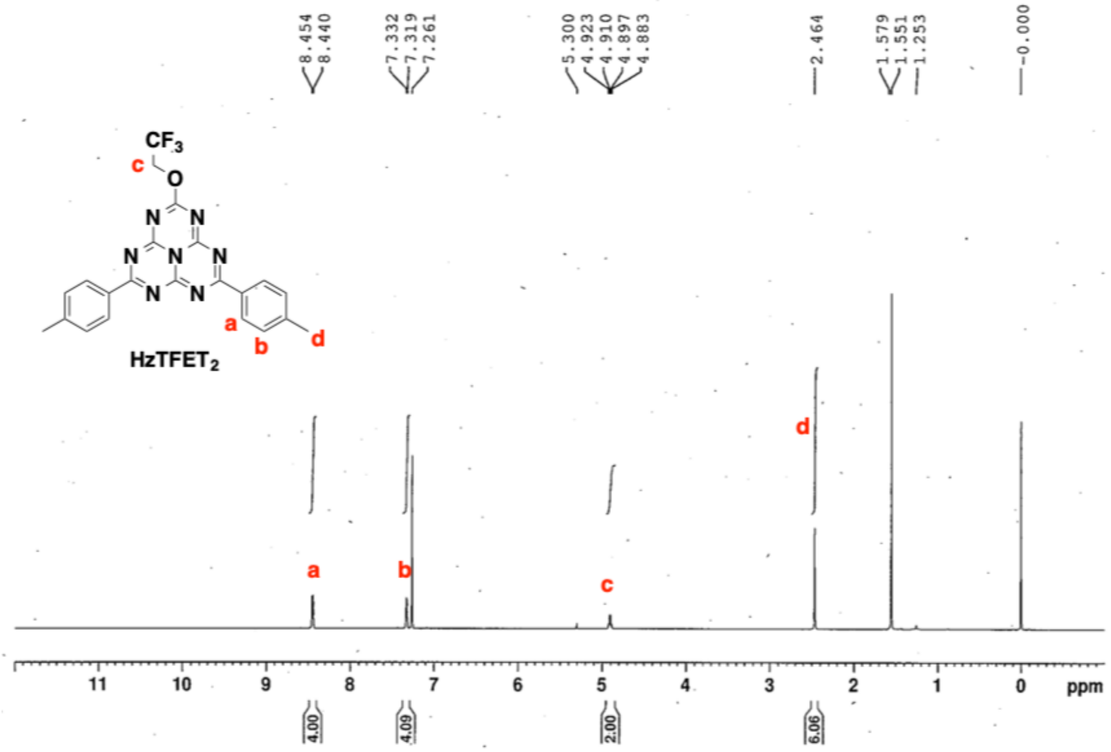
^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 1.68–1.72 (m, 6H), 2.36 (s, 6H), 2.67 (s, 6H), 3.96 (br s, 4H), 7.05–7.07 (br, 4H), 7.99 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ [ppm] = 21.81, 24.32, 26.19, 45.94, 129.16, 130.26, 132.01, 144.76, 156.53, 157.74, 161.11, 174.40. MS (FD-TOF): 464.24440 $[M]^+$, calcd. for $C_{25}H_{24}N_8$ (464.24369), error = 1.53 ppm.



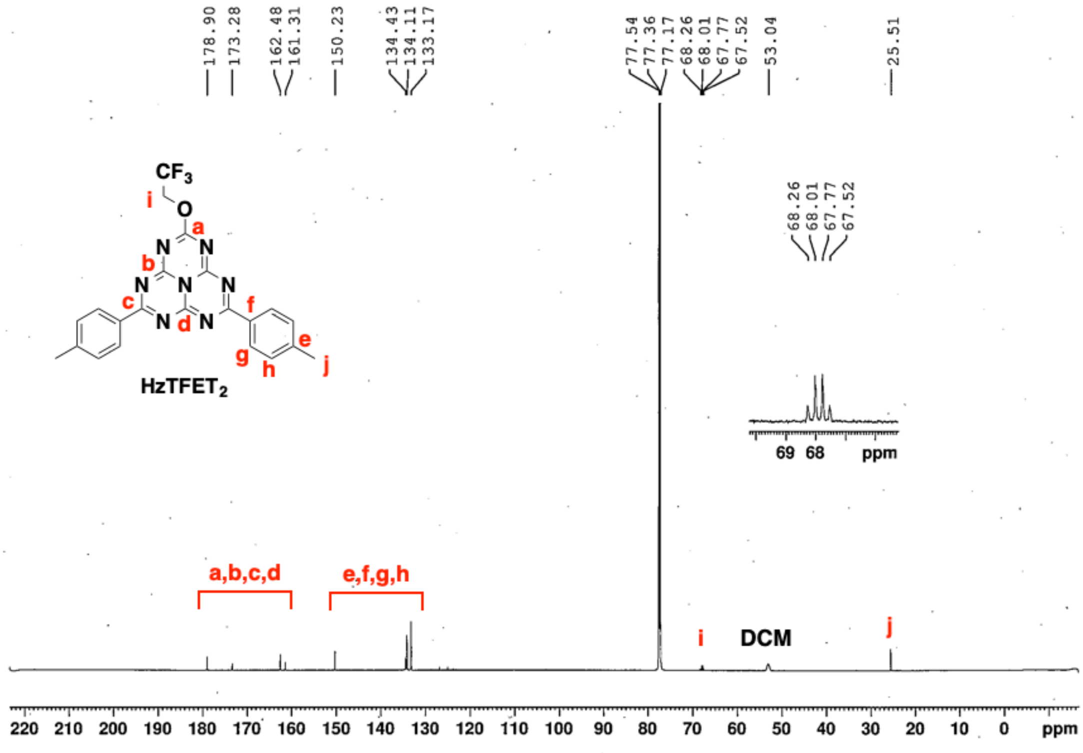
^{1}H NMR of **HzTFEX$_2$** in CDCl3 at 25 °C



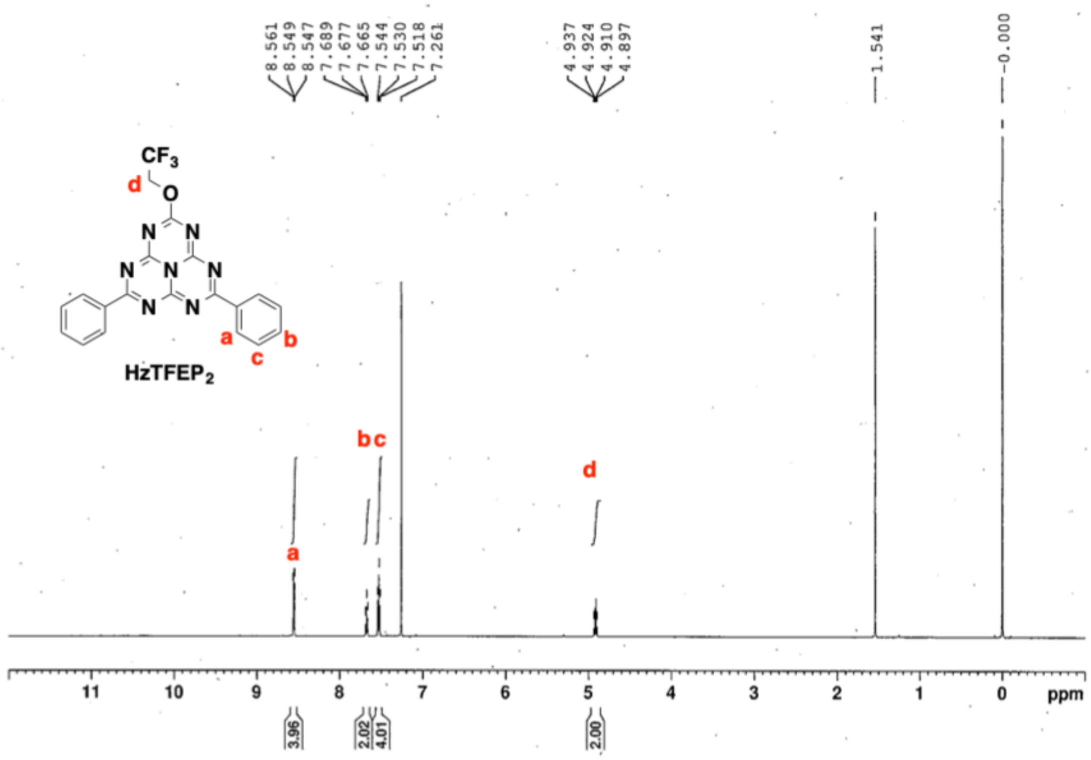
^{13}C NMR of **HzTFEX$_2$** in CDCl3 at 25 °C



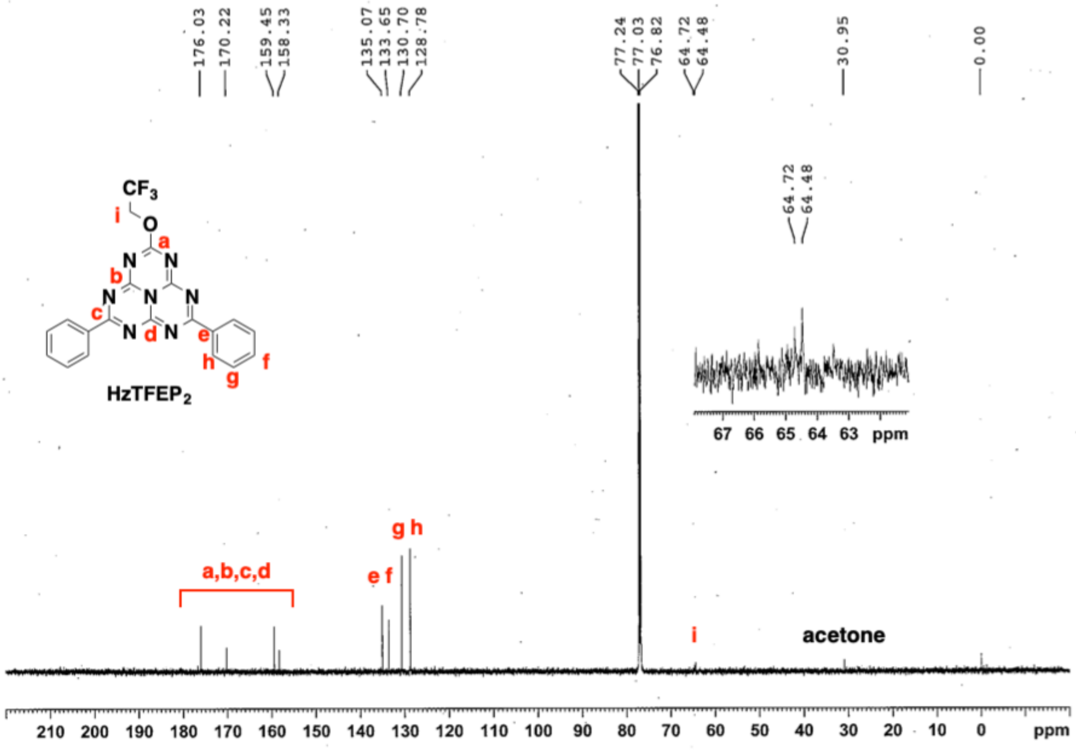
^{1}H NMR of **HzTFET$_2$** in CDCl3 at 25 °C



^{13}C NMR of **HzTFET$_2$** in CDCl3 at 25 °C



^{1}H NMR of **HzTFEP$_2$** in CDCl3 at 25 °C



^{13}C NMR of **HzTFEP$_2$** in CDCl3 at 25 °C

2. Supplementary materials and methods

Materials Commercially available reagents and solvents were used without further purification unless otherwise noted. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) aqueous dispersions were purchased from Heraeus. 2,4,5,6-Tetra(carbazol-9-yl)isophthalonitrile (4CzIPN), 4,4′′-bis(triphenylsilyl)-1,1′:4′,1′′-terphenyl (BST), bis(4-(dibenzo[*b*,*d*]furan-4-yl)phenyl)diphenylsilane (DBFSiDBF), bis(diphenylphosphoryl)dibenzo[*b*,*d*]furan (PPF), and 1,3-bis(3,5-di(pyridine-3-yl)phenyl)benzene (B3PyPB) were purchased from Luminescence Technology Corporation. 1,1-Bis(4-di-*p*-tolylaminophenyl)cyclohexane (TAPC), 4,4′-bis(carbazol-9-yl)biphenyl (CBP), tris(8-hydroxyquinolinato)aluminium (Alq3), 8-hydroxyquinolinatolithium (Liq), and 2-methyl-9,10-bis(naphthalene-2-yl)anthracene (MADN) were purchased from e-Ray Optoelectronics Technology. Molybdenum oxide (MoO_3), lithium fluoride (LiF), and aluminium (Al) were purchased from FURUUCHI Chemical.

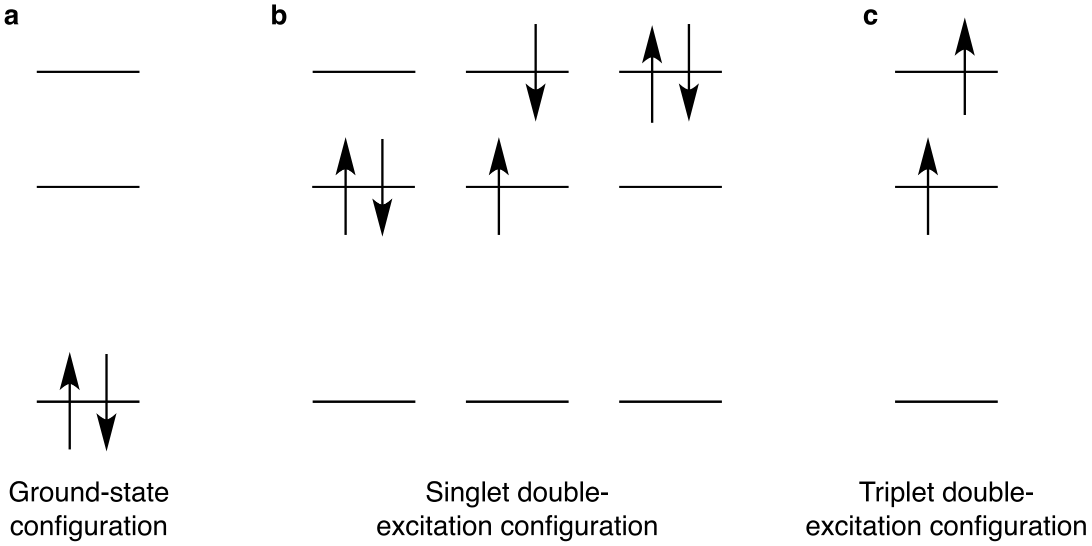
General method NMR spectra were recorded on a Bruker Avance III HD spectrometer. The chemical shifts (δ in ppm) were determined using tetramethylsilane as an internal reference. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker model AutoflexTM speed spectrometer in reflector mode using dithranol as a matrix. High-resolution mass data were obtained by using a JEOL JMS-T100GCV with field desorption (FD) as an ionization method.

OLED fabrication OLEDs were fabricated on glass substrates covered with indium tin oxide (ITO) (sheet resistance = 15 Ω sq^{-1}). The substrates were sequentially cleaned by sonication in detergent, deionized water, acetone, and 2-propanol, followed by UV–ozone treatment for 30 min. PEDOT:PSS was spin-coated on the substrates and annealed at 200 °C on a hot plate for 10 min in ambient conditions. The other materials were sequentially deposited on the substrates under vacuum ($< 5 \times 10^{-5}$ Pa) at a deposition rate of < 0.3 nm s^{-1} through shadow masks defining a pixel size of 4.0 mm^2. The deposition rate and layer thicknesses of each layer were monitored using a quartz crystal microbalance. The devices were prepared for evaluation by encapsulation using epoxy glue and glass lids under a nitrogen atmosphere. The fabricated OLEDs consist of the following layer sequences:

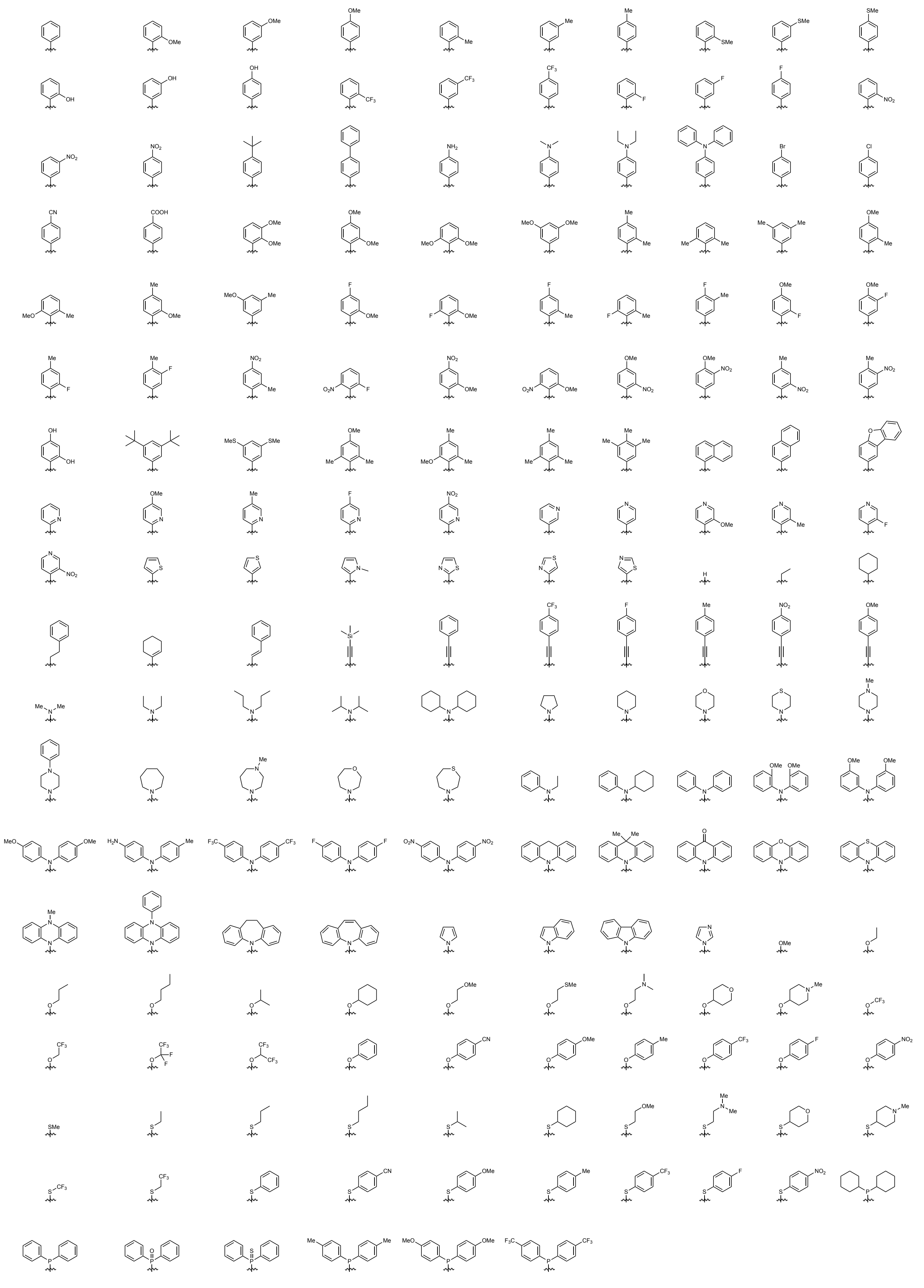
Device I. Glass/ITO (130 nm)/PEDOT:PSS (30 nm)/MoO_3 (5 nm)/BST (3 nm)/DBFSiDBF (10 nm)/PPF:10 wt% $HzTFEX_2$ (15 nm)/PPF (10 nm)/Alq3 (40 nm)/Liq (1 nm)/Al (80 nm)

Device II. Glass/ITO (130 nm)/PEDOT:PSS (30 nm)/TAPC (40 nm)/CBP:5 wt% 4CzIPN (20 nm)/B3PyPB (40 nm)/LiF (1 nm)/Al (80 nm)

Device III. Glass/ITO (130 nm)/PEDOT:PSS (30 nm)/TAPC (40 nm)/MADN (20 nm)/B3PyPB (40 nm)/LiF (1 nm)/Al (80 nm)



Supplementary Fig. 1 | Electronic configurations for two electrons in three orbitals. a, Ground-state configuration. **b,** Singlet double-excitation configurations. **c**, Triplet double-excitation configuration. The Pauli exclusion principle precludes the two electrons from occupying a given orbital in (c).

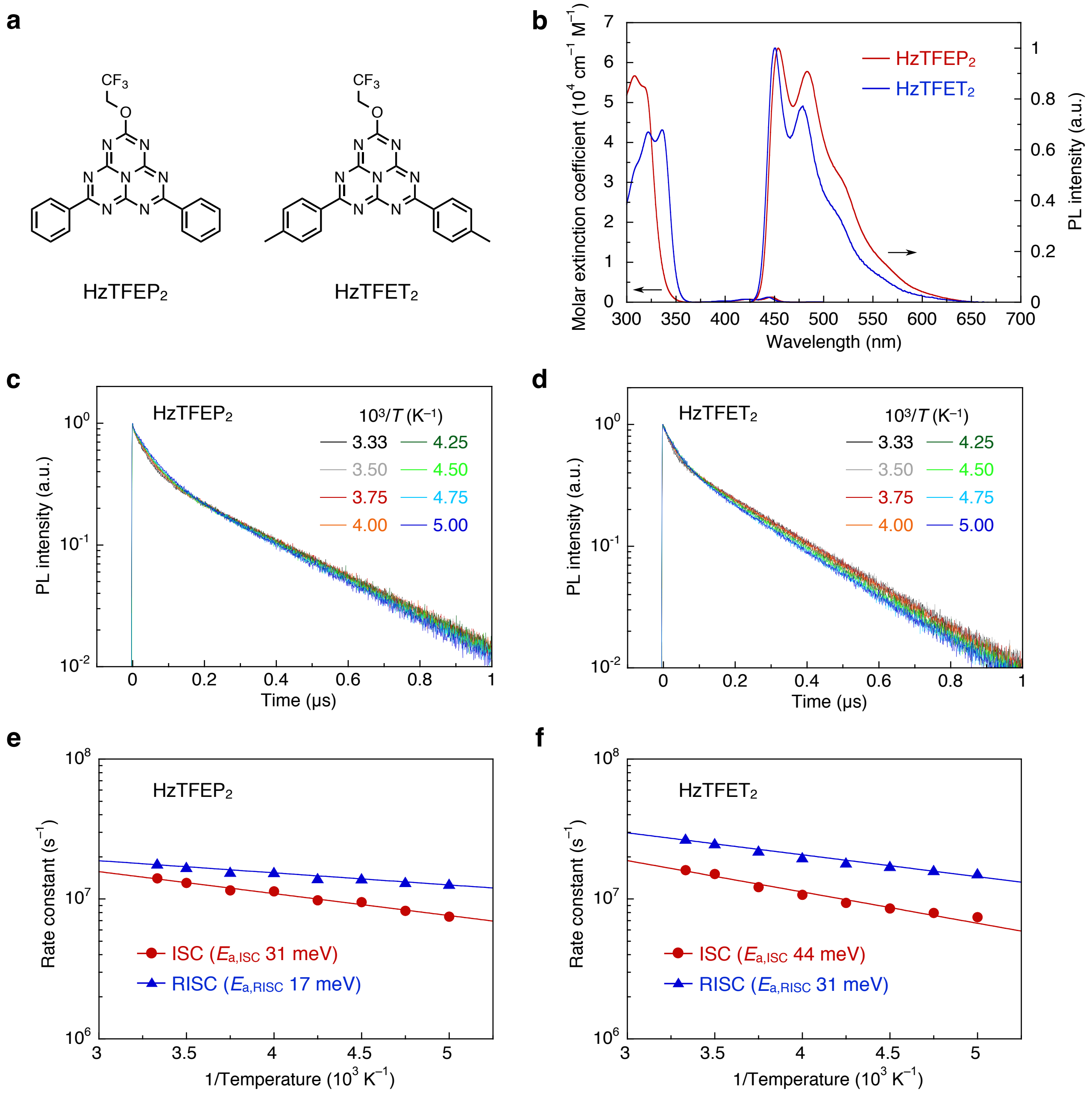


Supplementary Fig. 2 | Structures of 186 substituents used for generating the candidate heptazine analogues.

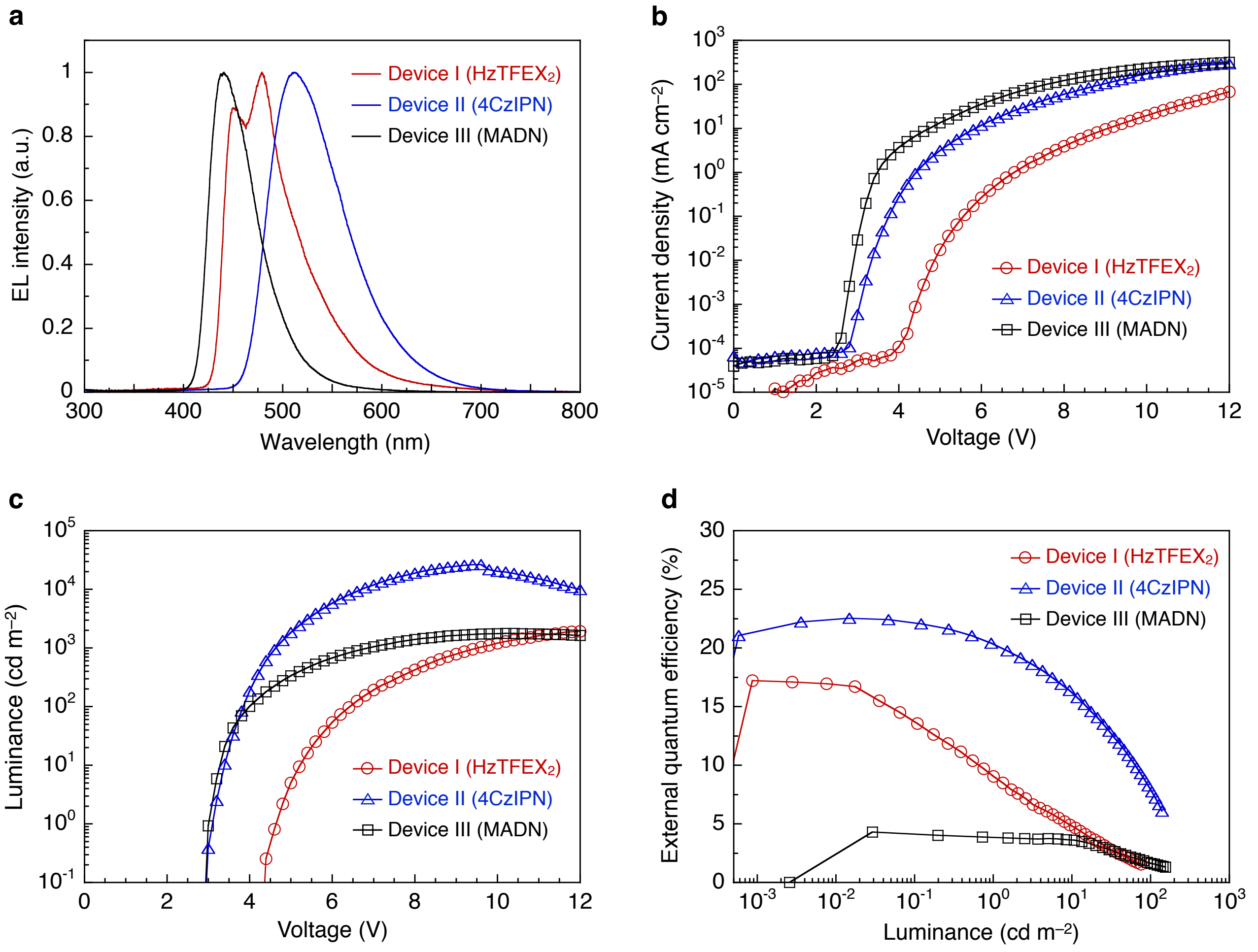
Supplementary Table 1 Singlet–triplet energy gap (ΔE_{ST}) and oscillator strength (f) of $\mathrm{HzTFEX_2}$ and $\mathrm{HzPipX_2}$ calculated by various methods.

Molecule	Method	ΔE_{ST} (meV)	f
$\mathrm{HzTFEX_2}$	TDDFT[a]	210	0.010
	EOM-CCSD[b]	–12	0.019
	ADC(2)[c]	–34	0.018
	CASPT2[d]	–184	–
$\mathrm{HzPipX_2}$	TDDFT[a]	334	0.015
	EOM-CCSD[b]	10	0.040
	ADC(2)[c]	–12	0.040
	CASPT2[d]	–171	–

[a] TDDFT LC-BLYP/6-31G(d) at the lowest-energy triplet excited state (T_1) geometry optimised by LC-BLYP/6-31G with a range-separated parameter of 0.18 bour^{-1}. [b] EOM-CCSD/cc-pVDZ at the T_1 geometry optimised by MP2/cc-pVDZ. [c] ADC(2)/cc-pVDZ at the T_1 geometry optimised by MP2/cc-pVDZ. [d] CASPT2(12,12)/cc-pVDZ at the T_1 geometry optimised by MP2/cc-pVDZ.



Supplementary Fig. 3 | Photophysical properties of HzTFEP$_2$ and HzPipT$_2$. a, Molecular structures of HzTFEP$_2$ and HzTFET$_2$. **b**, Steady-state absorption and photoluminescence (PL) spectra of HzTFEP$_2$ and HzTFET$_2$ in deaerated toluene. **c**, **d**, Transient PL decays of HzTFEP$_2$ (c) and HzTFET$_2$ (d) at varying temperatures in deaerated toluene. **e**, **f**, Temperature dependence of the rate constants of ISC and RISC (k_{ISC} and k_{RISC}) of HzTFEP$_2$ (e) and HzTFET$_2$ (f). The solid lines in (e) and (f) represent the fits of the plots to the Arrhenius equation.



Supplementary Fig. 4 | OLED performance. a, **b**, **c**, **d**, Electroluminescence (EL) spectra measured at 1.0 mA (a), current density–voltage characteristics (b), luminance–voltage characteristics (c), and external quantum efficiency–current density characteristics (d) of Devices I, II, and III.

Supplementary Table 2 Summary of OLED performance.

Device	Emitter	λ_{EL} (nm)[a]	CIE (x, y)[b]	V_{on} (V)[c]	$\eta_{\mathrm{ext,max}}$ (%)[d]	$\eta_{\mathrm{ext,1/100/1000}}$ (%)[e]
I	HzTFEX$_2$	450, 479	0.17, 0.24	4.8	17.2	17.1/10.3/4.2
II	4CzIPN	512	0.28, 0.56	3.2	22.5	21.4/22.0/19.7
III	MADN	441	0.15, 0.08	3.2	4.3	4.3/3.7/2.0

[a] Peak wavelength of EL spectra measured at 1.0 mA. [b] Commission Internationale de l'éclairage (CIE) coordinates measured at 1.0 mA. [c] Turn-on voltage for luminance > 1 cd m^{-2}. [d] Maximum external quantum efficiency. [e] External quantum efficiencies at luminances of 1, 100, and 1000 cd m^{-2}.