

A simple D- π -A hybrid mode for highly efficient non-doped blue OLEDs with CIE_y < 0.05 and EQE up to 6%

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Experimental section and methods

Cyclic voltammetry measurements: Cyclic voltammetry (CV) was performed using a BAS 100W (Bioanalytical Systems), using a glass carbon disk (diameter =3 mm) as the working electrode, a platinum wire with a porous ceramic wick as the auxiliary electrode, and Ag/Ag⁺ as the reference electrode standardized by the redox couple ferrocenium/ferrocene. Anhydrous *N,N*-dimethylformamide (DMF) and dichloromethane (CH₂Cl₂) containing 0.1 M tetrakis(*n*-butyl)-ammonium hexafluorophosphate (NBu₄PF₆) as the supporting electrolyte were used as solvents under a nitrogen atmosphere. All solutions were purged with a nitrogen stream for 10 min before measurements. The procedure was performed at room temperature, and a nitrogen atmosphere was maintained over the solution during measurements. A scan rate of 50 mV s⁻¹ was applied.

Lippert-Mataga model: The influence of solvent environment on the optical property of our compounds can be understood using the Lippert-Mataga equation, a model that describes the interactions between the solvent and the dipole moment of solute:

$$hc(\nu_a - \nu_f) = hc(\nu_a^0 - \nu_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3} f(\epsilon, n) \quad (1)$$

where f is the orientational polarizability of solvents, μ_e is the dipole moment of excited state, μ_g is the dipole moment of ground state; a is the solvent cavity (Onsager) radius, ϵ and n are the solvent dielectric and the solvent refractive index, respectively.

X-ray crystal structure data of TPATZ: TPATZ single crystal was successfully obtained by sublimation method. Single-crystal X-ray diffraction data were collected using a Rigaku RAXIS-PRID diffractometer with graphite monochromator Mo K α radiation. The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least squares on F^2 . Anisotropic thermal parameters were refined for all the non-hydrogen atoms. All the hydrogen atoms of ligands were generated geometrically. CCDC 1587403 containing the crystallographic

data can be obtained free from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The EQE measurement method for the non-doped device:

The measured parameters included luminance, current and EL spectrum. EQE was calculated according to the formula below:

$$EQE = \frac{\pi \cdot L \cdot e}{683 \cdot I \cdot h \cdot c} \cdot \frac{\int_{380}^{780} I(\lambda) \cdot \lambda d\lambda}{\int_{380}^{780} I(\lambda) \cdot K(\lambda) d\lambda} \quad (2)$$

where L (cd m^{-2}) is the total luminance of device, I (A) is the current flowing into the EL device, λ (nm) is EL wavelength, $I(\lambda)$ is the relative EL intensity at each wavelength and obtained by measuring the EL spectrum, $K(\lambda)$ is the Commission International de L'Eclairage chromaticity (CIE) standard photopic efficiency function, e is the charge of an electron, h is the Planck's constant, c is the velocity of light.

The radiative exciton ratio of the device: The theoretical value of the radiative excitons ratio was calculated by the following equation:

$$EQE = \gamma \times \phi_{PL} \times \eta_s \times \eta_{out} \quad (3)$$

where EQE is the external quantum efficiency; γ is the carrier recombination efficiency, which in the ideal case is supposed to be unity if the injected holes and electrons are fully recombined and degrade to excitons in the emissive layer, ϕ_{PL} is photoluminescence efficiency of the emission layer (~49% for TPATZ film); η_s is the radiative exciton ratio; and η_{out} is the light out-coupling efficiency (20-30%).

Supporting Figures

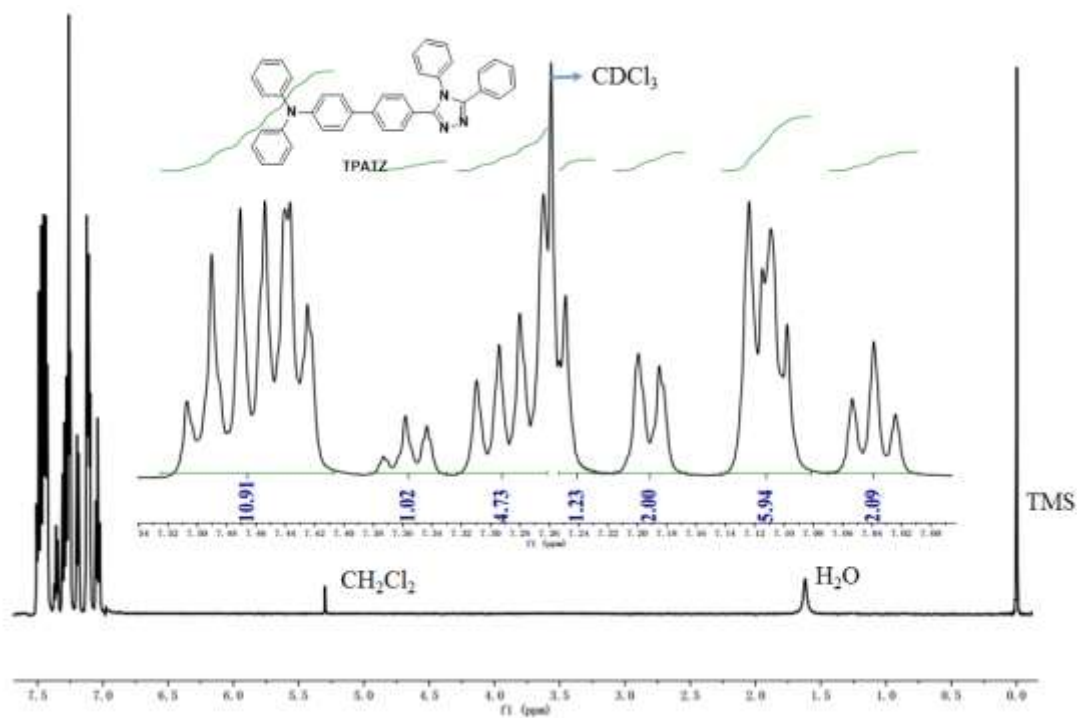


Figure S1. ¹H-NMR Spectrum of TPATZ in CDCl₃.

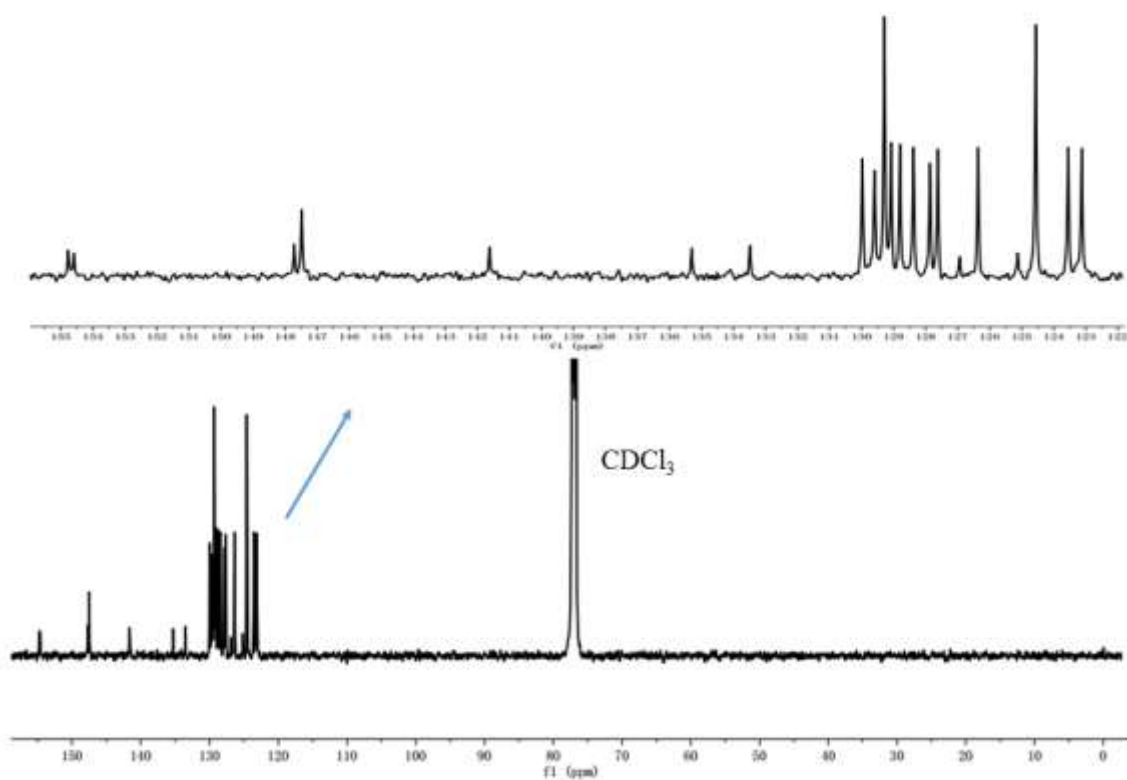


Figure S2. ¹³C-NMR Spectrum of TPATZ in CDCl₃.

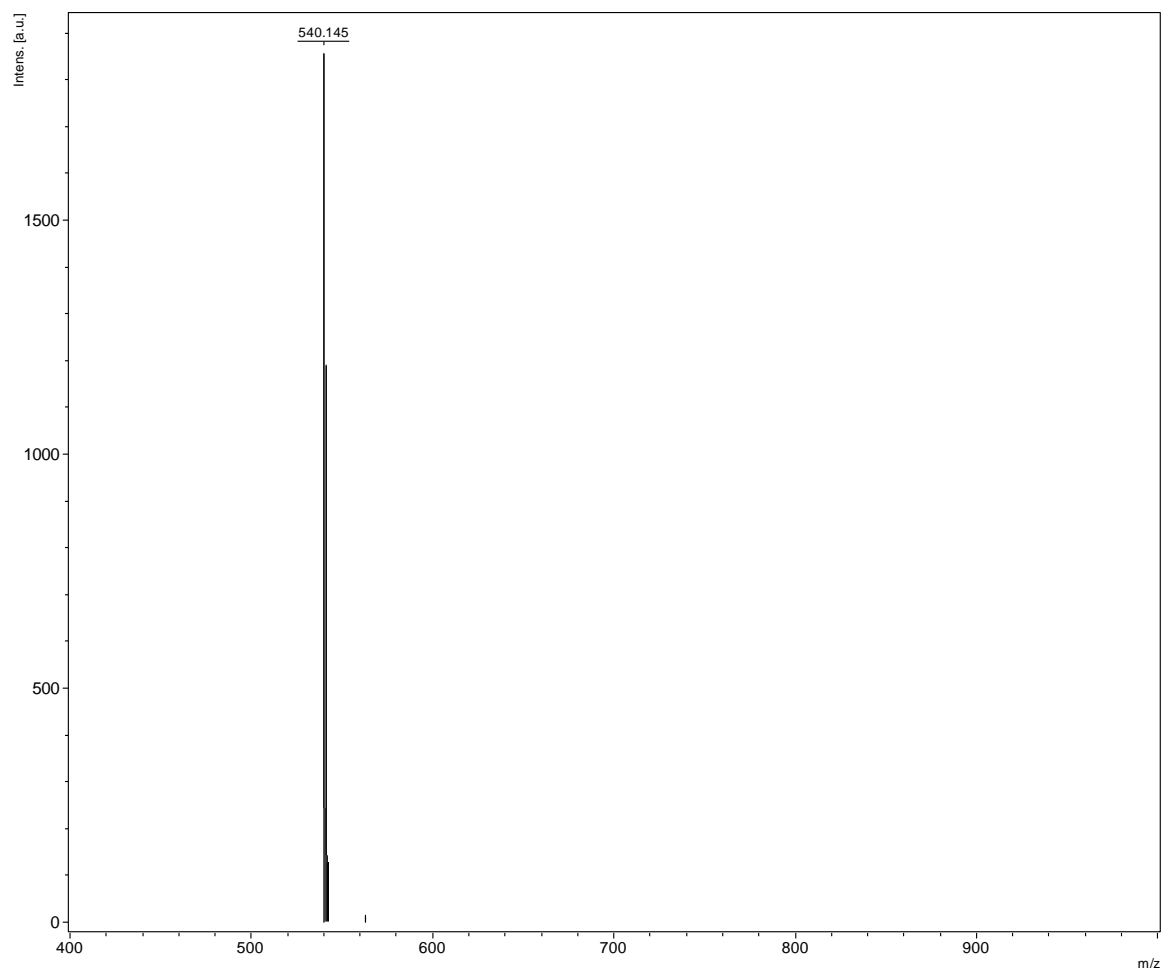


Figure S3. The time-of-flight mass spectrum of TPATZ.

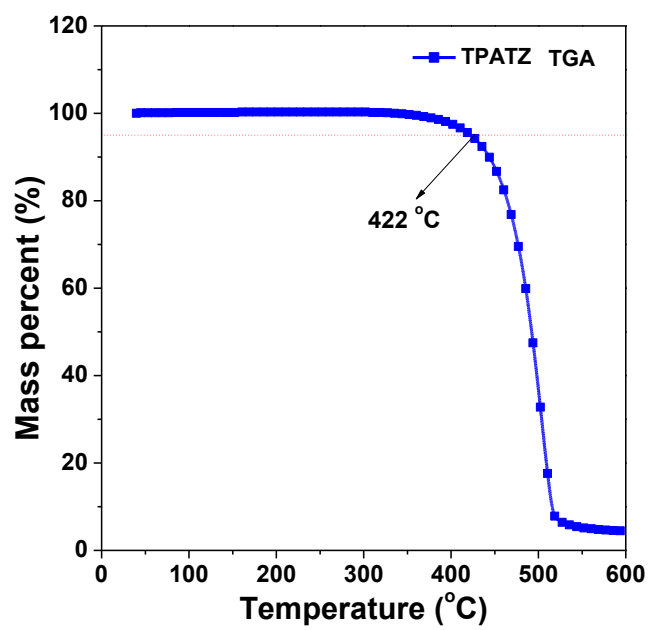


Figure S4. TGA curve of TPATZ.

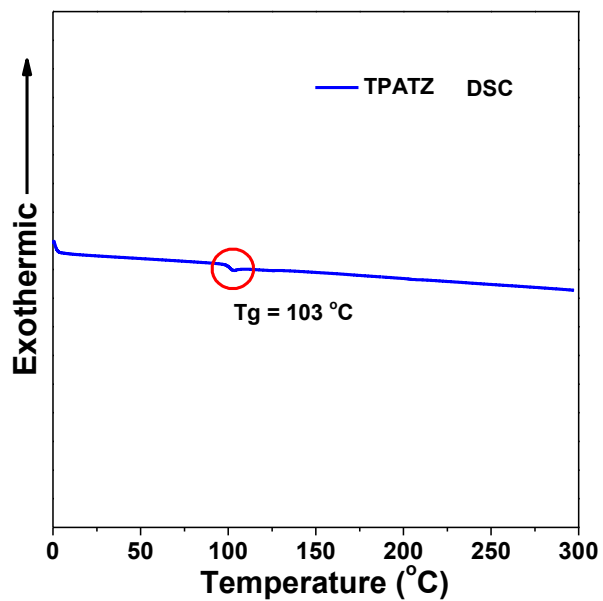


Figure S5. DSC curve of TPATZ.

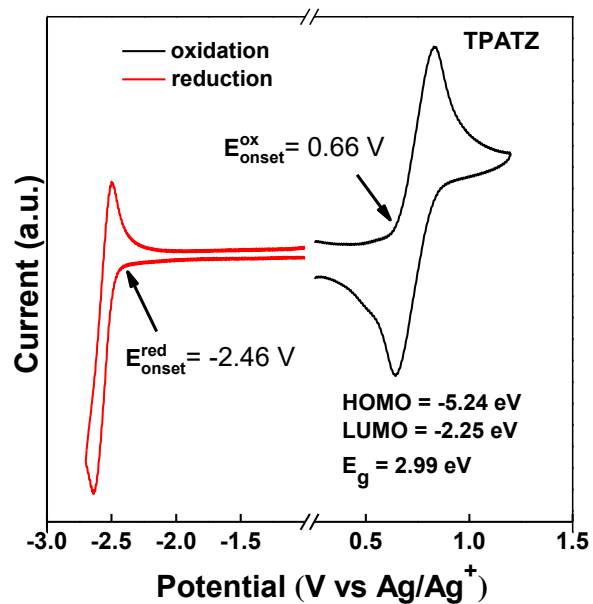


Figure S6. CV curve of TPATZ.

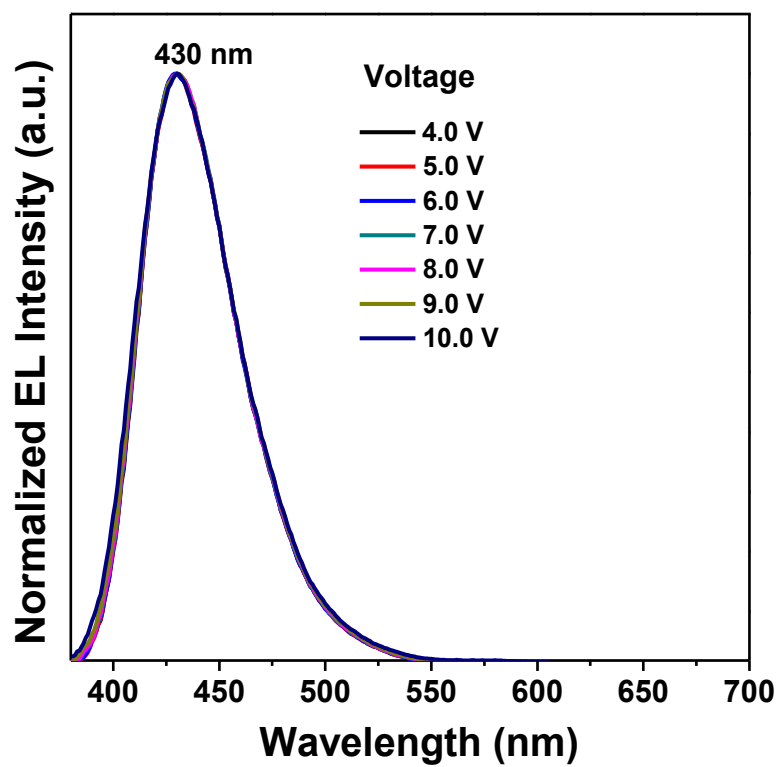


Figure S7. EL spectra at different voltages of non-doped device.

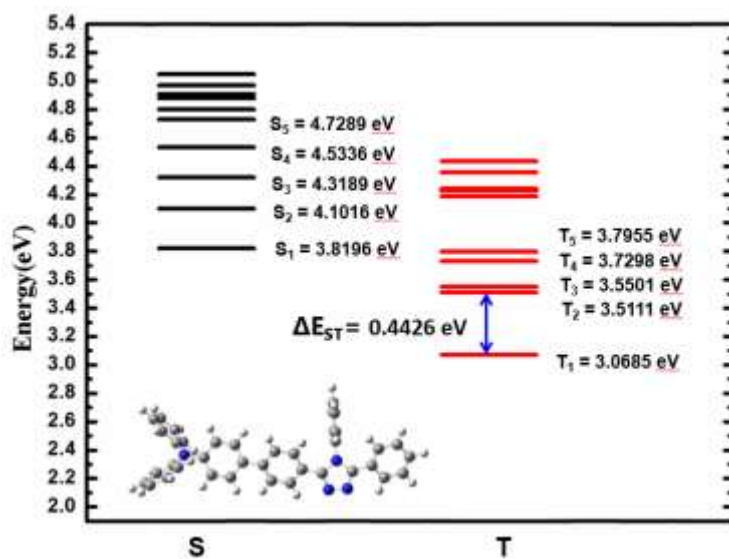


Figure S8. NTO for $S_0 \rightarrow S_1$ transition in TPATZ.

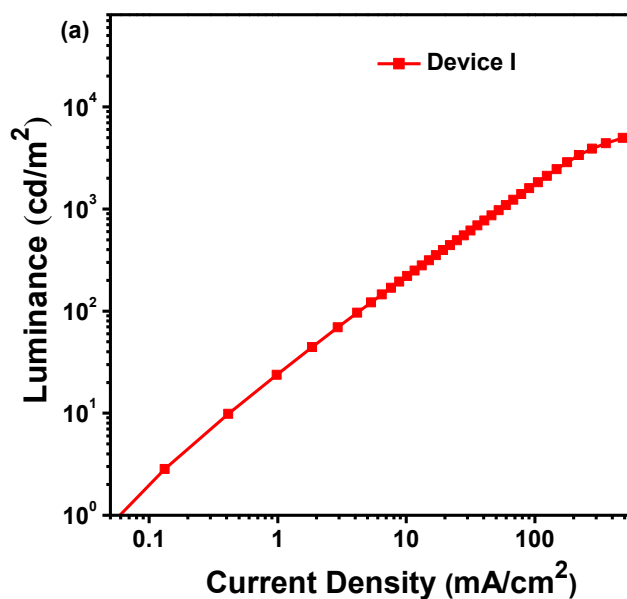


Figure S9. The luminescence-current density curve of the device (Device structure: ITO/HATCN (5 nm)/TAPC (50)/TPATZ (20 nm)/TPBi (55 nm)/LiF(1)/Al(100nm)).

Table S1 Single crystal structural parameters of TPATZ.

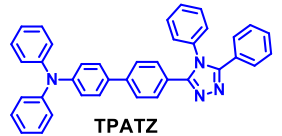
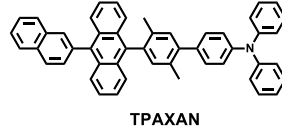
Compound reference	colorless TPATZ crystal
Chemical formula	C ₃₈ H ₂₈ N ₄
Formula weight	540.64
Crystal system	Triclinic
$a/\text{Å}$	9.632(7)
$b/\text{Å}$	16.037(12)
$c/\text{Å}$	19.704(15)
$\alpha/^\circ$	96.198(13)
$\beta/^\circ$	96.827(14)
$\gamma/^\circ$	107.054(13)
Unit cell volume/ Å^3	2856(4)
Temperature/K	296(2)
Space group	P-1
Z	4
Density (calculated) / g cm^{-3}	1.257
F(000)	1136
Theta range for data collection	1.05 to 25.00 deg.
Index ranges	$-10 \leq h \leq 11$, $-18 \leq k \leq 19$, $-22 \leq l \leq 23$
Reflections measured	14546
Independent reflections	9947

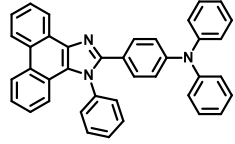
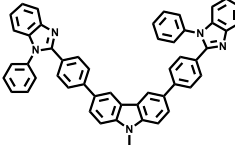
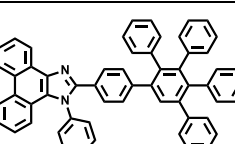
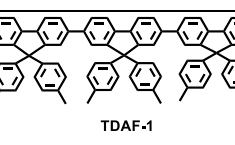
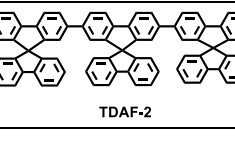
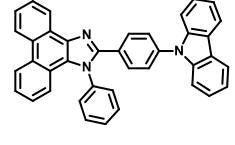
<i>R</i> _{int}	0.0354
Completeness to theta = 72.13°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9823 and 0.9758
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	9947 / 0 / 746
Goodness-of-fit on <i>F</i> ²	1.089
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0559
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1228
Final <i>R</i> _{<i>I</i>} values (all data)	0.1000
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1363
CCDC number	1587403

Table S2. The PL efficiency (Φ_{PL}) of TPATZ in different solvents.

solvent	n-hexane	isopropyl ether	diethyl ether	tetrahydrofuran	acetonitrile
Φ_{PL} (%)	60	77	86	92	86

Table S3. Recent representative non-doped true-blue OLEDs with $\text{CIE}_y \leq 0.05$ based on organic fluorescent small molecules.

Materials	V_{on} ^[a] [V]	CE_{max} ^[b] [cd A ⁻¹]	EQE_{max} ^[c] [%]	PE_{max} ^[d] [lm W ⁻¹]	λ_{EL} ^[e] [nm]	CIE [x, y]	ref
 TPATZ	3.1	2.41	5.92	2.20	430	0.155, 0.047	This work
 TPAXAN	3.4	–	4.62	–	428	0.155, 0.049	1

 <p>BPA-BPI</p>	2.0	0.65	1.37	0.68	428	0.15, 0.05	2
 <p>CPhBzIm</p>	2.5	1.6	3	1.07	426	0.16, 0.05	3
 <p>TTP-TPI</p>	3.1	2.10	5.02	1.88	424	0.16, 0.05	4
 <p>TDAF-1</p>	2.5	1.53	5.3	–	–	0.158, 0.041	5
 <p>TDAF-2</p>	2.5	1.1	4.1	–	–	0.160, 0.044	5
 <p>M1</p>	–	0.65	1.94	0.48	420	0.165, 0.050	6

^{a)}Turn on voltage at a luminance of 1 cd m⁻²; ^{b)}Maximal current efficiency; ^{c)}Maximal external quantum efficiency; ^{d)}Maximal power efficiency; ^{e)}Maximal EL peak value (λ_{EL}); e)Non-doped device.

Reference:

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