

Supporting information

Using azaacene as acceptor unit to construct ultraefficient red fluorophore with EQE over 40%

Xiao-Jing Wang,^{†a} Han Liu,^{†a} Kai Zhang,^{†b} Dezhi Yang,^c Ze-Hui Pan,^a Chuan-Kui Wang,^{*b} Man-Keung Fung^{a*}, Dongge Ma^{c*} and Jian Fan^{ad*}

^a *Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China*

^b *Shandong Province Key Laboratory of Medical Physics and Image Processing Technology, School of Physics and Electronics, Shandong Normal University, 250014 Jinan, China.*

^c *Institute of Polymer Optoelectronic Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, Guangdong-Hong Kong-Macao Joint Laboratory of Optoelectronic and Magnetic Functional Materials, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

^d *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 35002, China*

E-mail: ckwang@sdu.edu.cn, mkfung@suda.edu.cn, msdgm@scut.edu.cn, jianfan@suda.edu.cn

1. General Information

All reactions were performed under nitrogen atmosphere unless otherwise stated. Dry toluene (Tol) were purified by PURE SOLV (Innovative Technology) purification system. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and Agilent DD2-600 MHz NMR spectrometer at ambient temperature. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a Bruker ultraflex extreme MALDI-TOF spectrometer. UV-vis absorption spectra were recorded on Cary 60 spectrometer (Agilent Technologies). PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen. The glass transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature (T_d). Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene (Fc^+/Fc) as the external standard. The oxidative scans were performed using $0.1\text{ M } n\text{-Bu}_4\text{NPF}_6$ (TBAPF_6) in deoxygenated dichloromethane as the supporting electrolyte. A conventional three-electrode configuration consisting of a Pt-wire counter electrode, an Ag/AgCl reference electrode, and a Glassy-Carbon working electrode was used. The cyclic voltammograms were obtained at a scan rate of 0.1 V s^{-1} . All the calculations were carried out in Gaussian 16 package.

2. OLED fabrication and characterization

All the fabrication was based on the glass substrates pre-coated with 135 nm thick layer of indium tin oxide (ITO) ($15\text{ }\Omega/\text{sq}$). The ITO glass substrates were degreases ultrasonically in alternate baths of alcohol and de-ionized water, then they were dried in an oven at $100\text{ }^\circ\text{C}$ for 5 hours and treated by ultraviolet ozone for 15 minutes. Finally, followed by loaded into an evaporator, the device were fabricated under high vacuum of 4×10^{-6} Torr. The evaporation rates were controlled by oscillating quartz crystals. The evaporation rates of HAT-CN/Liq, other organic materials, and Al are 0.1-0.2, 1-2, and 4-6 $\text{\AA}/\text{s}$, respectively. The current density-voltage-luminance (J-V-L) characteristics and other electroluminescence (EL) information of the devices, such as

EL spectra, current efficiency (CE), and power efficiency (PE), were tested by the PR 745 photometer combined with a constant current source (Keithley 2400 SourceMeter). UV-vis absorption spectra were obtained from Lambda 750 spectrophotometer. Photoluminescence (PL) spectra were tested by a fluorescence spectrophotometer (Hitachi F-4600). Transient PL decays were measured on a Time resolved fluorescence spectrometer (PL-TCSPEC) of HORIB-FM 2015.

The EQE of the emission was obtained by measuring the light intensity in the forward direction and assuming the external emission profile to be Lambertian. Therefore, the EQE can be calculated using the following equations.^[2]

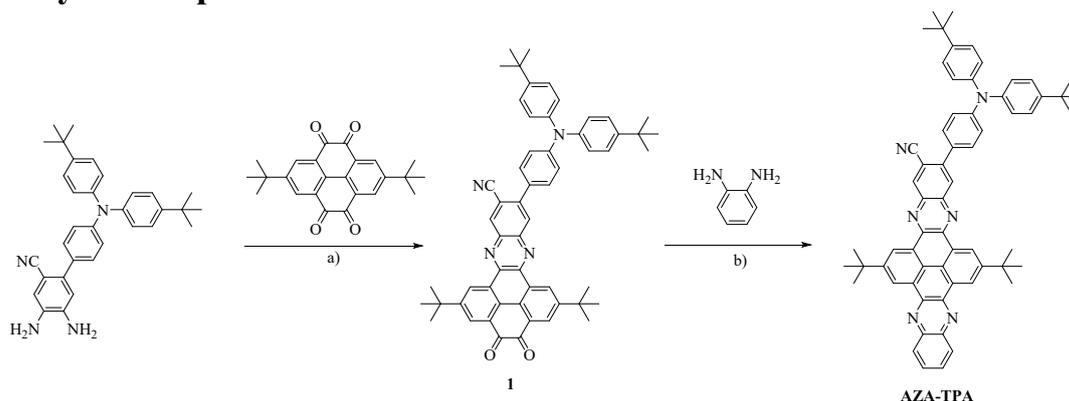
$$\text{EQE} = \frac{N_P}{N_E}$$

$$N_P = \frac{\int L_E(\lambda) \cdot W(\lambda) \cdot d\lambda}{h \times c} \times \pi \times D$$

$$N_E = \frac{I}{e}$$

Where N_E is the number of electrons, N_P is the number of photons, $L_E(\lambda)$ is spectral radiance ($\text{W sr}^{-1} \text{m}^{-2} \text{nm}^{-1}$), $W(\lambda)$ is wavelength, $d\lambda = 2$, D is emitting area, h is Planck's constant, e is the charge of an electron, c is the speed of light in vacuum and I is the current injected.

3. Synthetic procedure and characterization



Scheme S1. Synthetic procedure of **AZA-TPA** a) AcOH, 125 °C, 4h; b) AcOH, 125 °C, 2h.

12-(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)-2,7-di-tert-butyl-4,5-dioxo-4,5-dihydrophenanthro[4,5-abc]phenazine-11-carbonitrile (**1**)

4,5-diamino-4'-(bis(4-(tert-butyl)phenyl)amino)-[1,1'-biphenyl]-2-carbonitrile (100 mg, 0.21 mmol) and 2,7-di-tert-butylpyrene-4,5,9,10-tetraone (235 mg, 0.63 mmol) were suspended in AcOH (150 mL) and heated at 130°C for 4h under nitrogen. After cooling to room temperature, the solution was poured into cold water. The solid was filtered off and washed with water, and then dried under vacuum. The crude product was purified by column chromatography with DCM/PE (1:1, v/v) and then was recrystallized in methanol to afford compound **1** (110 mg, 63.42%). ¹H NMR (300 MHz, CDCl₃) δ 9.64 (d, J = 2.5 Hz, 2H), 8.89 (s, 1H), 8.66 (s, 2H), 8.48 (s, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.4 Hz, 4H), 7.17 (dd, J = 16.4, 8.5 Hz, 6H), 1.58 (s, 18H), 1.35 (s, 18H). MALDI-TOF-MS: m/z calcd for C₅₇H₅₄O₂N₄: 826.42, found: 826.54.

7-(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)-2,11-ditertbutylquinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine-6-carbonitrile (**AZA-TPA**)

Compound **1** (100 mg, 0.12 mmol) and benzene-1,2-diamine (13 mg, 0.12 mmol) were suspended in AcOH (50 mL) and heated at 130°C for 2h under nitrogen. After cooling to room temperature, the solution was poured into cold water. The solid was filtered off and washed with water, and then dried under vacuum. The crude product was purified by column chromatography with DCM/PE (1:2, v/v) and then recrystallized in methanol to afford compound **AZA-TPA** (82 mg, 76.10%). ¹H NMR

(600 MHz, CDCl₃) δ 9.80 (d, *J* = 5.3 Hz, 2H), 9.72 (d, *J* = 9.3 Hz, 2H), 8.86 (s, 1H), 8.45 (s, 1H), 8.42 (dd, *J* = 9.6, 3.6 Hz, 2H), 7.92-7.86 (m, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 4H), 7.17 (dd, *J* = 25.7, 8.6 Hz, 6H), 1.56(s, 18H), 1.35(s, 18H).
MALDI-TOF-MS: m/z calcd for C₅₇H₅₄O₂N₄: 898.47, found: 898.83.

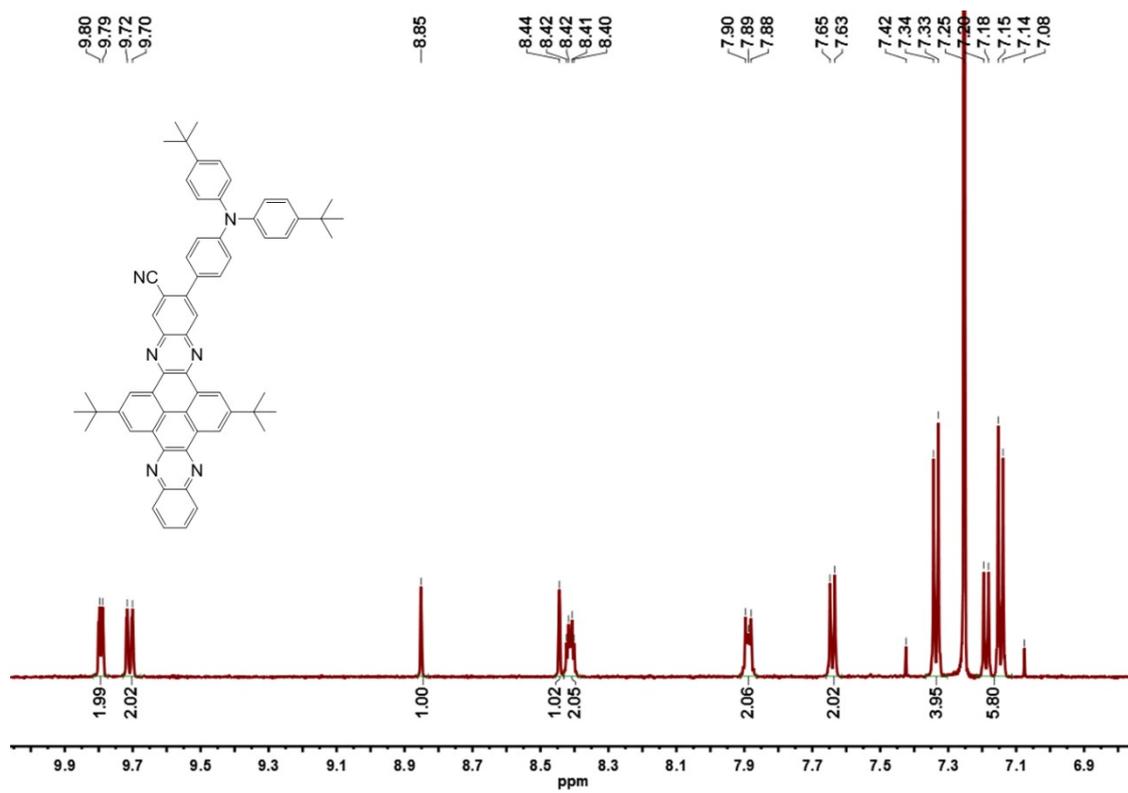


Fig. S1 ¹H NMR spectrum (CDCl₃, 600 MHz) of AZA-TPA.

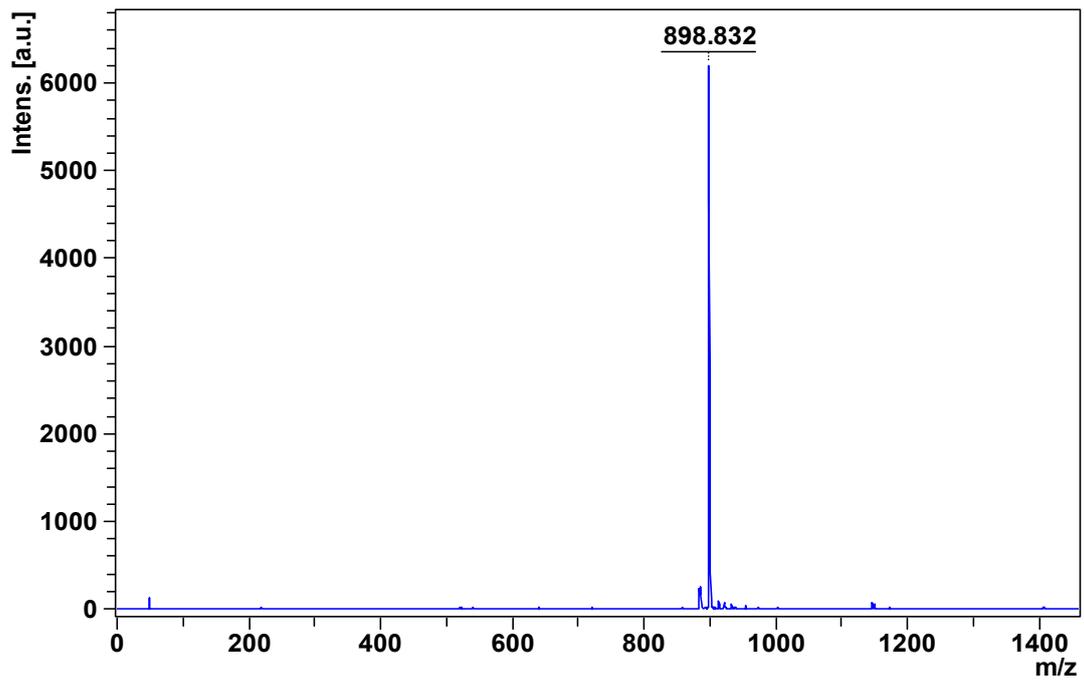


Fig. S2 MALDI-TOF-MS spectrum of AZA-TPA.

4. Electrochemical and thermal and properties

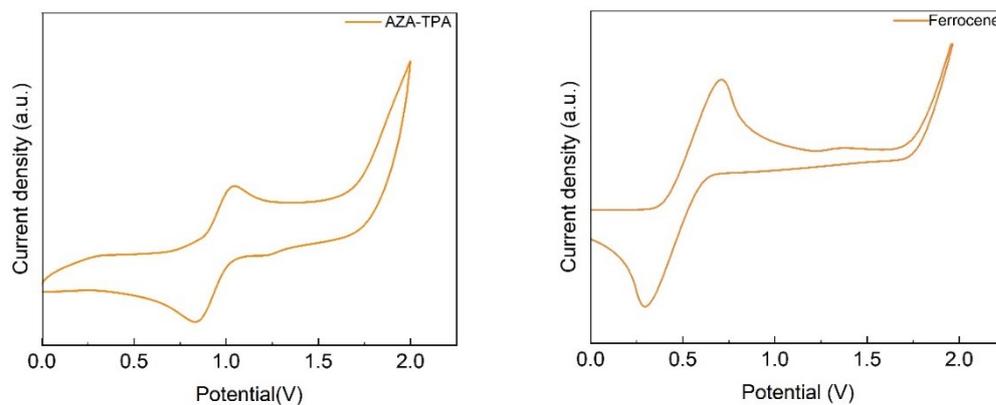


Fig. S3 Cyclic voltammograms of AZA-TPA and Ferrocene.

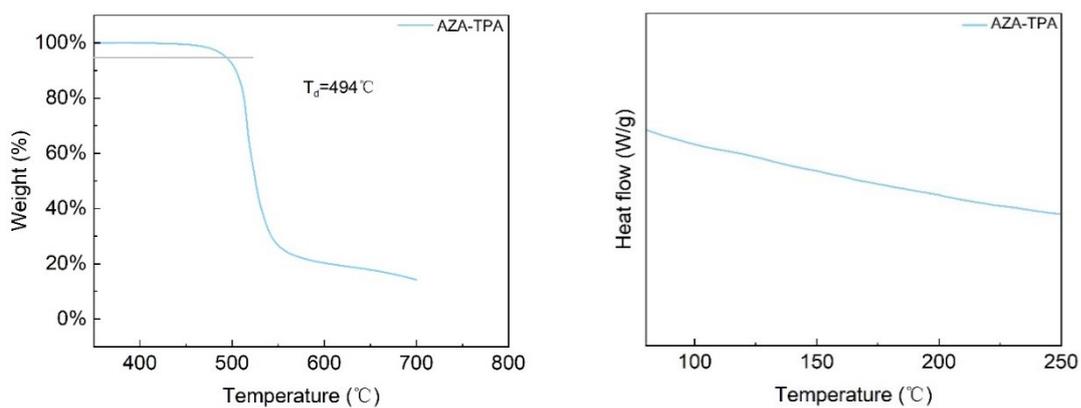


Fig. S4 TGA (left) and DSC (right) curves of AZA-TPA at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 .

5. Photophysical properties

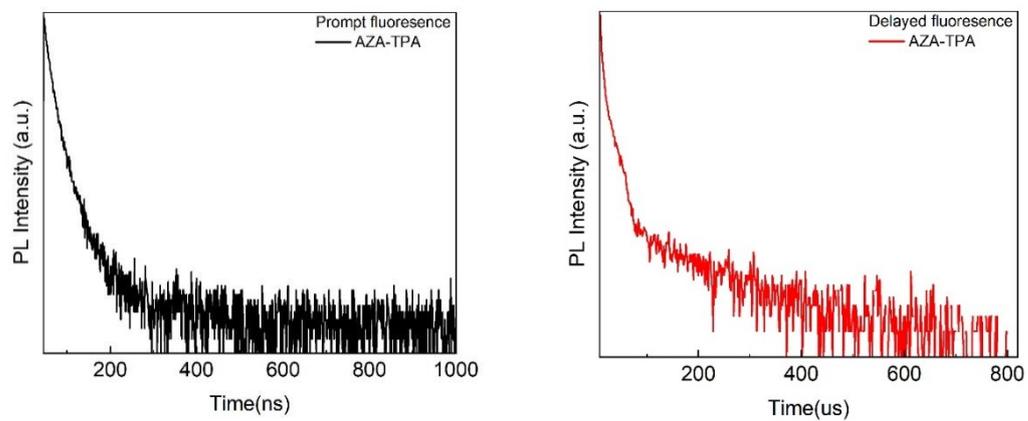


Fig. S5 Transient PL decay curves of AZA-TPA in doped CBP film (6 wt%).

6. Calculation formulas for the photophysical parameters

Ignoring singlet internal conversion (IC) process, the main rate constants were determined by using the following equations: Ignoring singlet internal conversion (IC) process, the main rate constants were determined by using the following equations:

$$k_p = \frac{1}{\tau_p}$$

$$k_d = \frac{\Phi_d}{\tau_d \Phi_{ISC}}$$

$$k_r^S = \Phi_p \cdot k_p$$

$$k_{ISC} = k_p - k_r^S$$

$$k_{RISC} = \frac{k_p \cdot k_d \cdot \Phi_d}{k_{ISC} \cdot \Phi_p}$$

$$k_{nr}^T = k_d - \left(1 - \frac{k_{ISC}}{k_r^S + k_{ISC}}\right) \cdot k_{RISC}$$

$$\Phi_{ISC} = 1 - \Phi_p$$

Φ_{PL} is the absolute photoluminescence quantum yield; Φ_p is the prompt fluorescent component of Φ_{PL} ; Φ_d is the delayed fluorescent component of Φ_{PL} ; τ_p is the lifetime of prompt fluorescent; τ_d is the lifetime of delayed fluorescent; k_p is the rate constant of prompt fluorescence decay; k_d is the rate constant of delayed fluorescence decay; k_r^S is the rate constant of radiative transition from S_1 to S_0 ; k_{ISC} is the rate constant of intersystem crossing; k_{RISC} is the rate constant of reverse intersystem crossing; k_{nr}^T is the non-radiative decay rate constant from T_1 to S_0 ; Φ_{ISC} is the quantum efficiency of intersystem crossing process.

Table S1 Photophysical characteristics of AZA-TPA in CBP (6 wt%).

Compound	Φ_{PL} [%]	$\Phi_{\text{p}}/\Phi_{\text{d}}$ [%]	τ_{p} [ns]	τ_{d} [μs]	k_{p} [10^8 s^{-1}]	k_{d} [10^3 s^{-1}]	k_{r}^{S} [10^7 s^{-1}]	k_{ISC} [10^7 s^{-1}]	k_{RISC} [10^4 s^{-1}]	k_{nr}^{T} [10^2 s^{-1}]
AZA-TPA	87.0	23.5/63.5	9.3	158.2	1.1	5.3	2.5	8.2	1.9	8.9

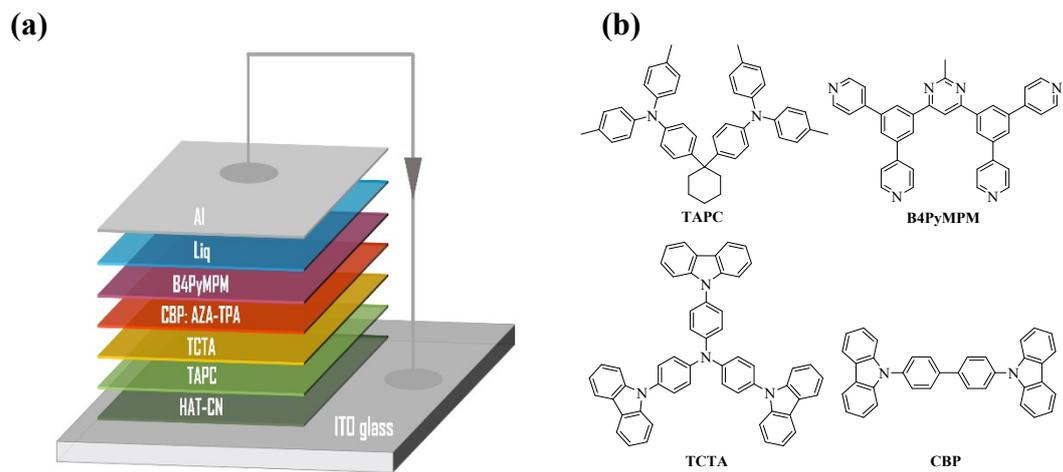


Fig. S6 (a) Schematic diagram of the device structure. (b) Molecular structures of the materials employed in the devices.

Table S2 Electroluminescence characteristics for the devices based on AZA-TPA

Emitter	Dopant ratio	$V_{on}^a)$ (V)	$L_{max}^b)$ (cd/m ²)	CE ^{c)} (cd/A)	PE ^{d)} (lm/W)	$\lambda_{max}^e)$ (nm)	EQE ^{f)} (%)	CIE ^{g)} (x, y)
AZA-TPA	3 wt%	2.45	4272	73.68	101.08	610	41.30	(0.54, 0.46)
	6 wt%	2.40	4101	61.00	88.72	618	39.68	(0.56, 0.44)
	9 wt%	2.30	1546	39.23	58.68	622	32.17	(0.59, 0.41)
	12wt%	2.20	1411	28.24	40.33	626	25.88	(0.60, 0.40)

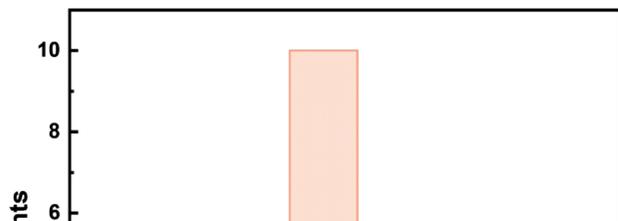


Fig. S7 Device reproducibility out of 26 trials of 3% AZA-TPA-doped devices.