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Supporting Information

Isolated Asymmetric Bilateral Steric Conjugated Polymers with Thickness-Independent Emission for Efficient and Stable Light-emitting Optoelectronic Devices

Ning Sun,[a†] Yuqin Liu,[ac†] Lili Sun,[a†] Yamin Han,[a] Xiang An,[a] Man Xu,[a] Chen Sun,[a] Jinyi Lin,*[ac] Lubing Bai,[a] Bo Li,[b] Chuanxin Wei,[a] Chengrong Yin,*[a] Mengna Yu,[b] Qi Wei,[c] Xuehua Ding,[a] Zongqiong Lin,[c] Yuyu Liu,*[b] Dong Guo,[b] Xinwen Zhang,[b] Linghai Xie [bc] and Wei Huang*[abc]

[a]Center for Supramolecular Optoelectronics (CSO), Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China. E-mail: iamjylin@njtech.edu.cn., iamcryin@njtech.edu.cn, wei-huang@njtech.edu.cn.
[b]Center for Molecular Systems and Organic Devices (CMSOD), Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China. E-mail: iamyyliu@njupt.edu.cn
[c]Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, Shaanxi, China.

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Supplementary Materials

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- **EXPERIMENTAL SECTION**

Chemicals

All chemicals were purchased from commercial suppliers unless otherwise specified, and used as received unless stated otherwise. Anhydrous THF (HPLC grade) was collected from Solvent Purification Systems (Innovative Technology, Inc.).Anhydrous chloroform was pre-dried over molecular sieves.

Characterization

^{1}H- and ^{13}C-NMR spectrum was recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the interval standard. Thermogravimetric analyses (TGA)were conducted by a Shimadzu DTG-60H under a heating rate of 10 ^{o}C/min and a nitrogen flow rate of 50cm^3/min. DSC measurement was acquired using a Shimadzu Instruments DSC-60A.DSC date were collected from 30 to 328 ^{o}C at a rate of 10 ^{o}C /min for both of the baseline and sample. Gel permeation chromatography (GPC) analysis was performed on a HP1100 HPLC system equipped with 7911GP-502 and GP NXC columns using polystyrenes as the standard and tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 ml/min at 25 ^{o}C. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, Nanjing, Jiangsu, China) at room temperature, and emission spectra were recorded on a Shimadzu RF-5301(PC) luminescence spectrometer (Shimadzu Corporation, Nanjing, Jiangsu, China). Cyclic voltammetric (CV) studies were conducted using an CHI660C Electrochemical Work station in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag^+) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-}Bu_4NPF_6$) in CH_2Cl_2 at a sweeping rate of 0.1 V/s. According to the redox onset potentials of the CV measurements, the HOMO/LUMO = - [E_{onset}-$E_{(Fc/Fc^+)}$ + 0.48] eV. The PLQE was measured using an Edinburgh FLSP920 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe900). The film morphologies of polymer films were recorded with a Bruker's Dimension Icon AFM in tapping mode (Bruker's Sb/Si probe tip with a resonant frequency 320 kHz and the spring constant 42 Nm^{-1}).The thickness of polymer films were measured using a Bruker 129 Dektak XT stylus profiler. Raman microscopy was performed using a Renishaw 2000 CCD spectrometer coupled to an Olympus BH-2 confocal microscope, and using the 633 nm line of a He-Ne laser as the excitation source to avoid absorption and resonance effects. XRD spectra were recorded on a Rigaku X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å), and the operating 2θ angle ranged from 5^o to 30^o, with the step length of 0.025.

UV-vis and PL Spectroscopy

Samples were prepared by spin coating the toluene or chloroform polymer solutions onto cleaned quartz substrates. All absorption spectra were measured using a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, Nanjing, Jiangsu, China) and emission spectra were recorded on a Shimadzu RF-5301(PC) luminescence spectrometer (Shimadzu Corporation, Nanjing, Jiangsu, China). In order to compare the influence of different film thickness on the absorption and emission of PHPDPF-Cz, PHDPF-Cz, PODPF ,PF10 thin film, toluene solutions with different concentrations were prepared and the films were rotated at the same speed. In order to investigate the stability of four polymer films, two groups of films were prepared. One group of films were obtained by using 10 mg/ml of polymer toluene and chloroform solutions at different rotational speeds to obtain films of different thickness which were designed to investigate its stability after two weeks of aging. Another group of films that used to explore its stability under different temperature aging were prepared at the same concentration and speed, heated and aged for 10 minutes at different temperatures, and their absorption ang emission were measured every two days.

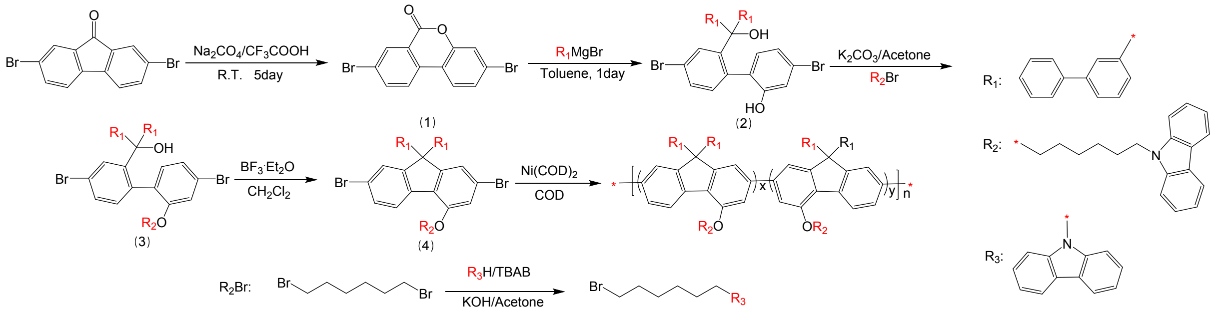
PLEDs fabrication

The structure of device is ITO/ PEDOT: PSS (PEDOT: PSS blended materials as electrode) / polymers film / TPBI / LiF / Al. A thin hole-injection layer (20nm) of PEDOT: PSS was spin-coated on the transparent conductive ITO at a spin speed of 1000 rpm for 78 s. After heating in air for 15 minutes, the emissive polymer layer was coated on the top of the PEDOT: PSS layer. Polymer films were spin-coated from their different concentrations of toluene solution which were used to obtain various film thicknesses. The background pressure of the chamber was under 10^{-6} Torr during the deposition process. EL spectra and CIE coordinates of the devices were used Spectra Scan PR655 spectra radiometer to measure. All the devices were characterized without encapsulation under ambient condition. The device's current-voltage luminescence characteristics were recorded by Keithley source meter (model 2602) and PR655 spectra radiometer.

ASE and Laser Characterization:

For gain measurements, the configuration of planar waveguides based on F8BT was fabricated from 20 mg/ml CB solutions onto quartz substrates by spin-coating, while the concentration of FDFBT and FCzBT were 40 mg/mL. The corresponding film thicknesses were measured using a KLA Tencor P-7 profiler. The samples were optically pumped with a nitrogen laser delivering 800-ps pulses at a repetition rate of 10 Hz. The pulse energy incident on the sample was adjusted by insertion of calibrated neutral density filters into the beam path. The pump beam was focused with a cylindrical lens and spatially filtered through an adjustable slit to create a 400 μm × 4 mm excitation stripe on the sample. By pumping the films with a rectangular light stripe and collecting the emission from the edge of the films, the spontaneously emitted photons are waveguided inside the organic thin film by virtue of the optical slab waveguide structure formed by the film between air and the quartz substrate. The amplified emission effect manifests as emission spectral narrowing and an abrupt output intensity increase.

Supplementary Materials

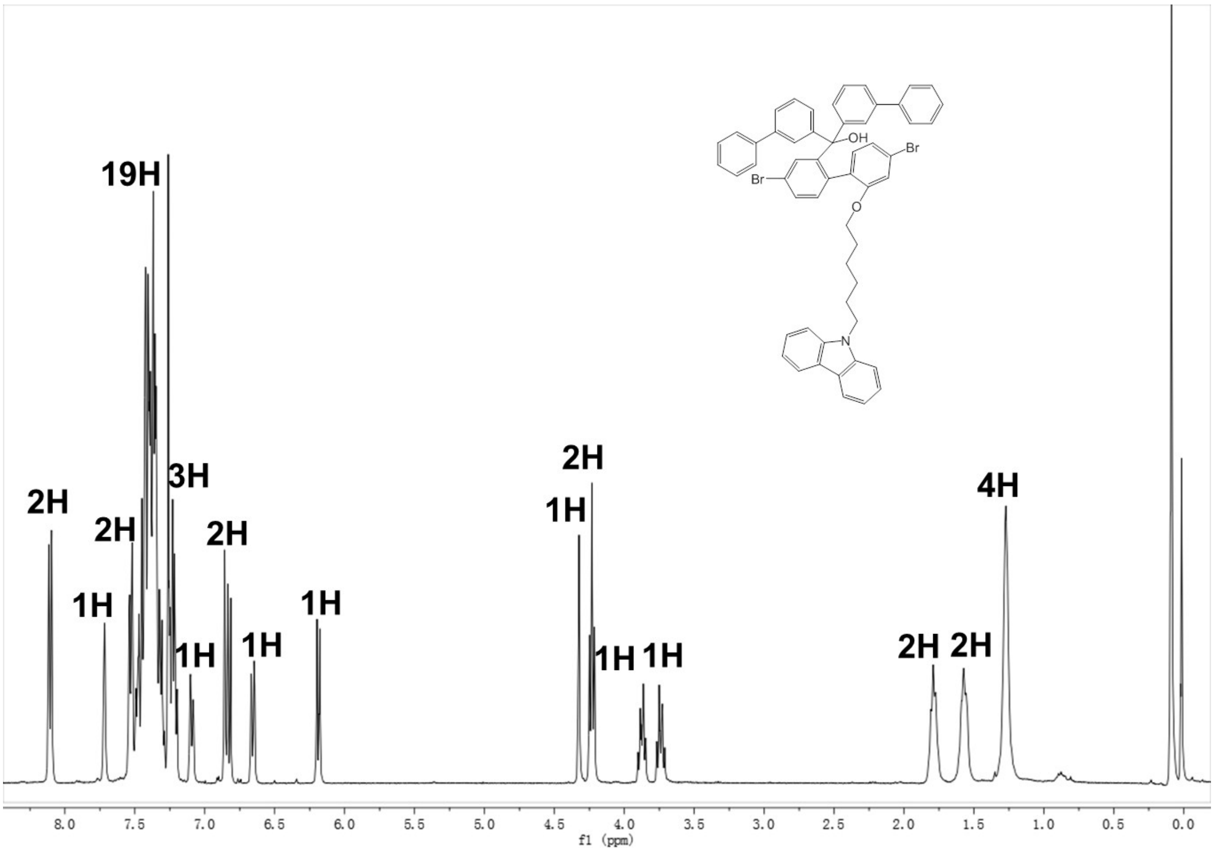


***Scheme* S1.** Synthetic routes of PHPDPF-Cz.

(2'-(6-(9H-carbazol-9-yl)hexyloxy)-4,4'-dibromo-[1,1'-biphenyl]-2-yl)diphenylmethanol (3). To a solution of K_2CO_3 (0.97 g, 7 mmol) and **(2)** (1.82 g, 2 mmol) in DMF (3 mL) was added dropwise 9-(6-bromohexyl)-9H-carbazole (0.79 g, 2.4 mmol). The mixture was heated to 70 ^{o}C for 24 hours in the dark under the nitrogen. After the solids were filtered off, the mother liquor was treated with 1 M HCl and petroleum ether. The water phase was extracted three more times with dichloromethane, and the combined extract was washed three times with 1 M HCl, then with water for three times. The mixture solution was dried with anhydrous $MgSO_4$. The solvents were removed by rotary evaporation, and the crude product was purified by column chromatography using petroleum ether: dichloromethane=3:1 as eluent to provide a white solid (1.274 g, yield 70%). MALDI-TOF-MS (m/z): 759.44 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.132-8.076 (d, 2H, Ar H), 7.735-7.699 (s, 1H, Ar H), 7.549-7.511 (m, 2H, Ar H), 7.501-7.282 (m, 19H, Ar H), 7,249-7.186 (m, 3H, Ar H), 7.116-7.070 (d, 1H, Ar H), 6.870-6.804 (m, 2H, Ar H), 6.681-6.636 (m, 1H, Ar H), 6.213-6.165 (dd, 1H, Ar H), 4.339-4.307 (s, 1H, OH H), 4.263-4.201 (m, 2H, OCH_2 H), 3.909-3.839 (m, 1H, CH_2 H), 3.775-3.700 (m, 1H, CH_2 H), 1.840-1.737 (m, 2H, CH_2 H), 1.612-1.532 (m, 2H, CH_2 H), 1.304-1.237 (m, 4H, CH_2 H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 155.632, 148.503, 147.104, 146.273, 141.581, 141.520, 141.069, 140.971, 140.648, 136.293, 134.521, 133.030, 132.671, 130.831, 129.951, 128.984, 128.573, 128.253, 127.539, 127.063, 126.718, 126.454, 126.082, 125.989, 125.892, 123.570, 123.064, 122.035, 121.684, 120.635, 119.033, 115.453, 108.921, 82.097, 69.160, 43.018, 29.119, 28.887, 26.992, 25.856.

9-(6-((9,9-di([1,1'-biphenyl]-3-yl)-2,7-dibromo--9H-fluoren-4-yl)oxy)hexyl)-9H-carbazole (4) A solution of boron trifluoride–diethyl ether complex (0.15 mL) in appropriate dichloromethane (5 mL) was added dropwise to a solution of **(3)** 0.911 g (1 mmol) in appropriate dichloromethane (5 mL). The reaction mixture was stirred at r.t. (25 °C) for 24 hours. Ethanol (50 mL) and water (50 mL) was successively added to quench the reaction. And then the phases were separated and the aqueous phase was extracted with dichloromethane. The combined dichloromethane layers were washed and dried ($MgSO_4$). After removal of the solvent, the remaining crude product was purified by column chromatography using petroleum ether: dichloromethane=6:1 as eluent to provide white products. (0.884 g, yield 99%). MALDI-TOF-MS (m/z): 741.24 (M^+). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.170-8.116 (d, 2H, Ar H), 7.951-7.918 (d, 1H, Ar H), 7.565-7.266 (m, 24H, Ar H), 7.215-7.161 (m, 1H, Ar H), 6,993-6.959 (d, 1H, Ar H), 4.396-4.317 (t, 2H, OCH_2 H), 4.097-4.031 (t, 2H, OCH_2 H), 2.017-1.874 (m, 4H, CH_2 H), 1.639-1.484 (m, 4H CH_2 H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 155.445, 153.935, 152.299, 144.939, 141.443, 140.957, 140.371, 137.652, 130.910, 128.917, 128.726, 127.342, 127.203, 127.043, 126.821, 126.272, 126.144, 125.618, 125.214, 122.806, 122.152, 122.351, 120.926, 120.379, 118.787, 113.993, 108.582, 68.292,66.018, 42.875, 28.972, 27.016, 26.054.

Poly[4-(6-carbazol)-(hexyloxy)-[9,9-(3-phenyl)-diphenyl]-fluoren-2,7-duyl]-*co*-[5-(6-carbazol)-(hexyloxy)-[9,9-(3-phenyl)-diphenyl]-fluoren-2,7-diyl] (PHPDPF-Cz) 0.45 g (0.5 mmol) was added to a appropriate DMF (10 mL) and toluene (10 ml) solution containing $Ni(COD)_2$ 0.33 g (2.4 equiv) 1,5-cyclooctadiene 0.15 mL (2.4 equiv), and bpy 0.186 g (2.4 equiv) in a 50 mL Schlenk tube under argon. The reaction mixture was stirred for 36 h at 90 °C to obtain a dark blue solution. The bromobenzene was added to solution for terminating reaction. After the mixture had cooled to room temperature, 10ml THF and 1.0 ml hytrazine hydrate of was added for quenching activator. The precipitate was separated by filtration. The solution should further purification to be subjected to alumina (Al_2O_3) column chromatography eluting with THF to afford PHPDPF-Cz as a green-yellow powder (268 mg, 90%). (GPC: M_n 2.12 × 10^4, M_w 4.02 × 10^4, PDI 1.89. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.17-8.02 (3H, Ar H), 7.67-7.45 (4H, Ar H), 7.44-7.01 (11H, Ar H), 7.24-7.07 (13H, Ar H), 4,32-4.25 (2H, CH_2 H), 4.15-3.94 (2H, CH_2 H), 1.95-1.81 (4H, CH_2 H), 1.59-1.45 (4H, CH_2 H).



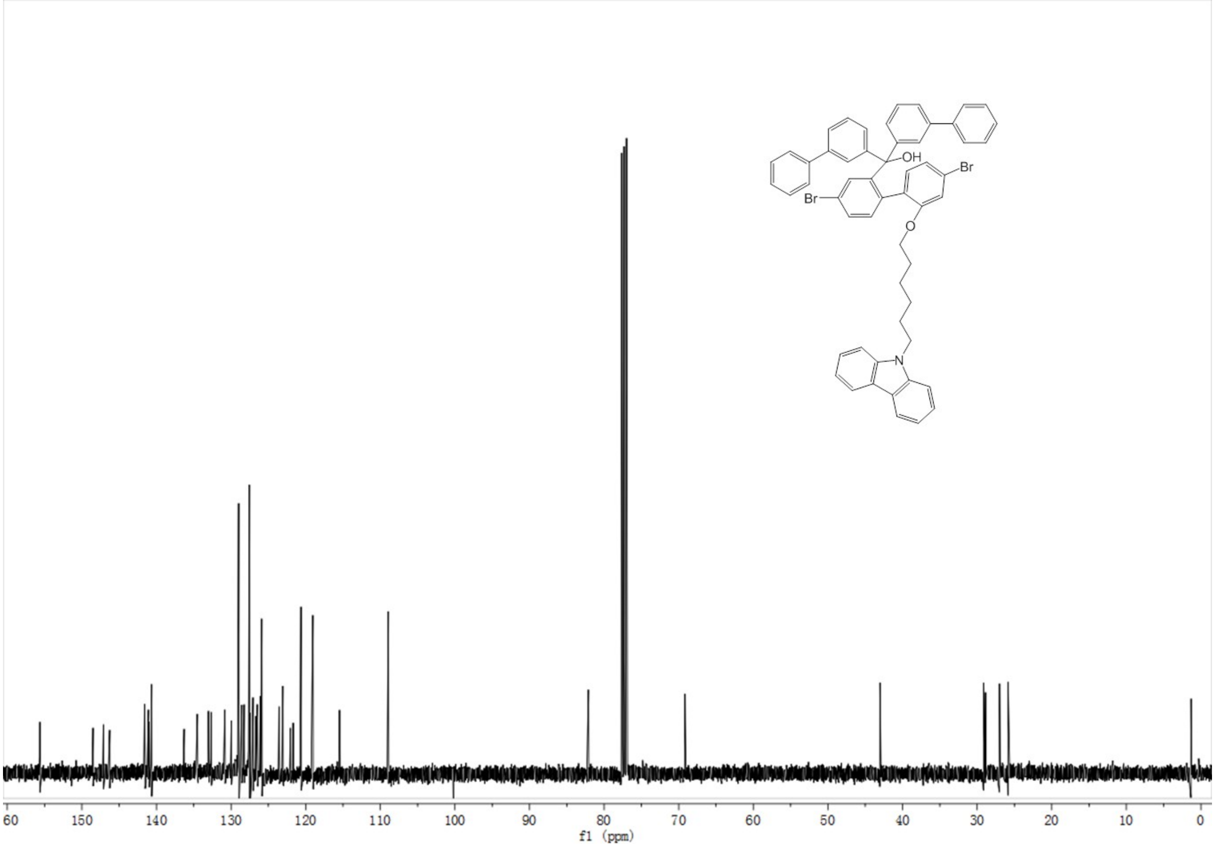
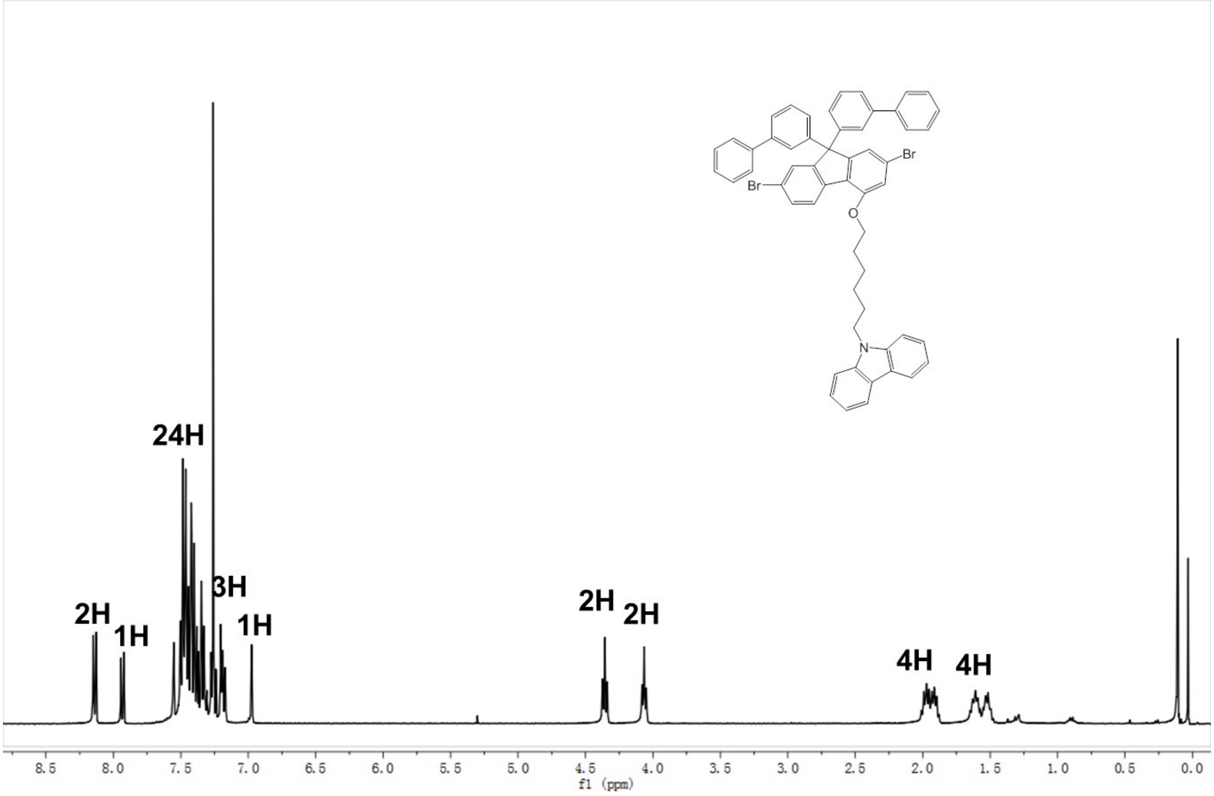


Figure S1-1. ^{1}H and ^{13}C spectra of 3



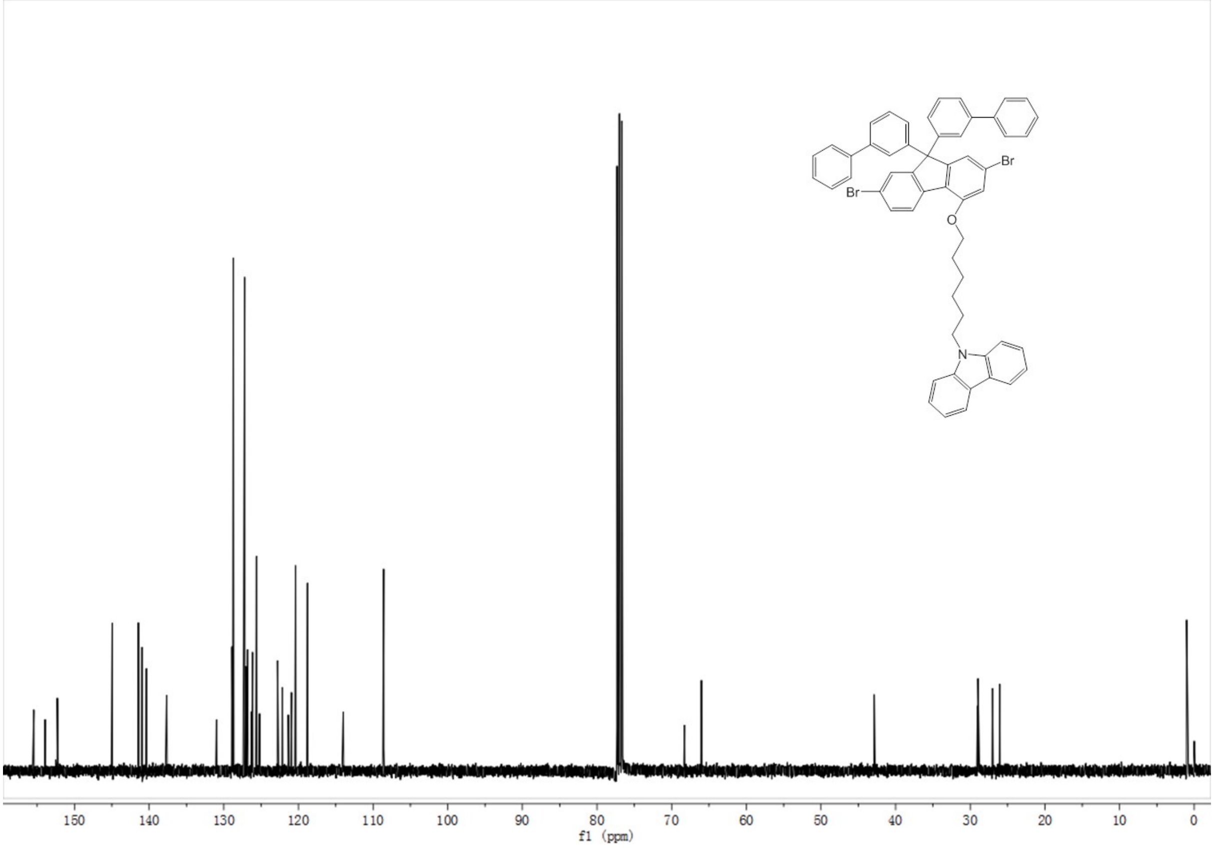


Figure S1-2. ^{1}H and ^{13}C spectra of Monomer, DBrHPDPF-Cz.

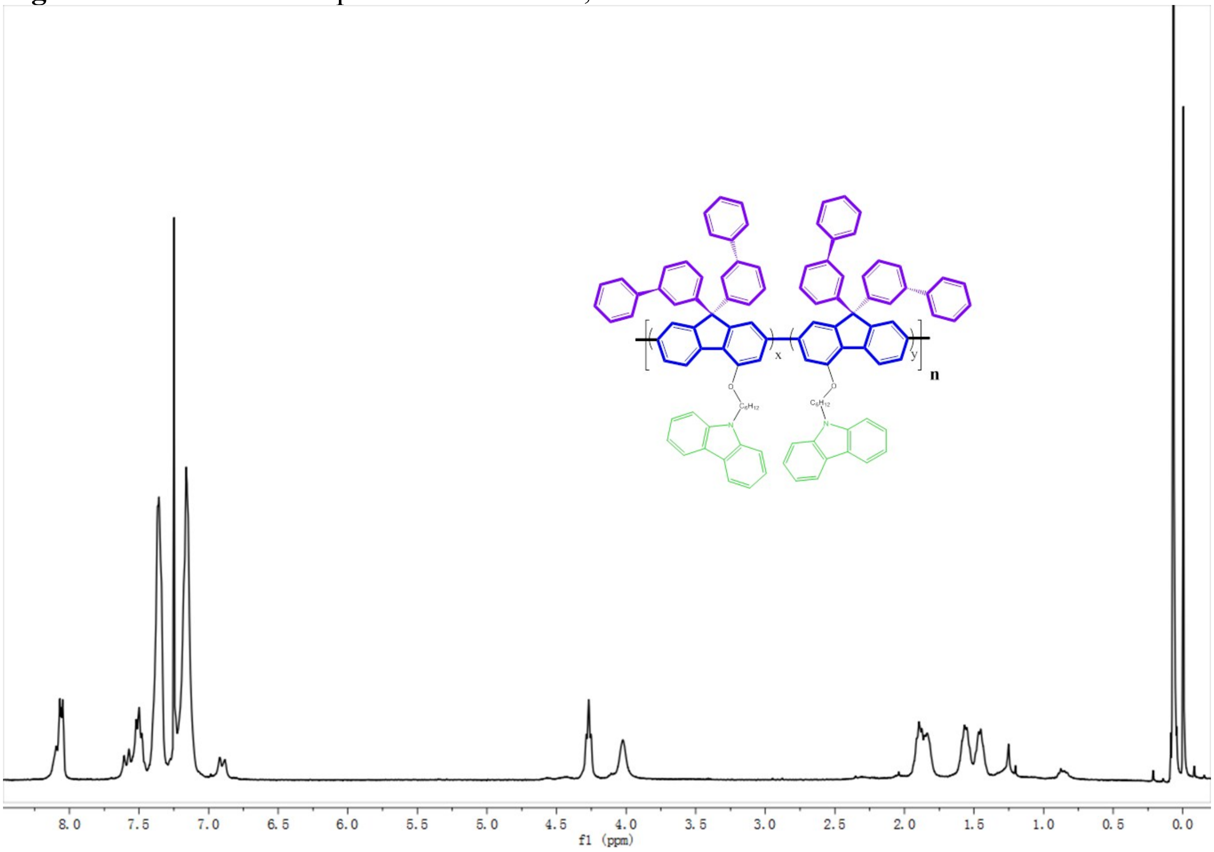


Figure S1-3. ^{1}H spectra of PHPDPF-Cz.

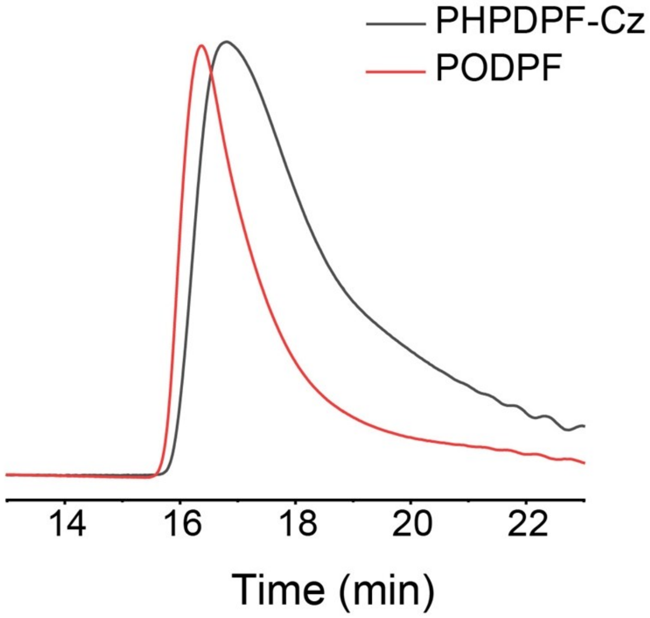


Figure S2. GPC curves of PHPDPF-Cz and PODPF.

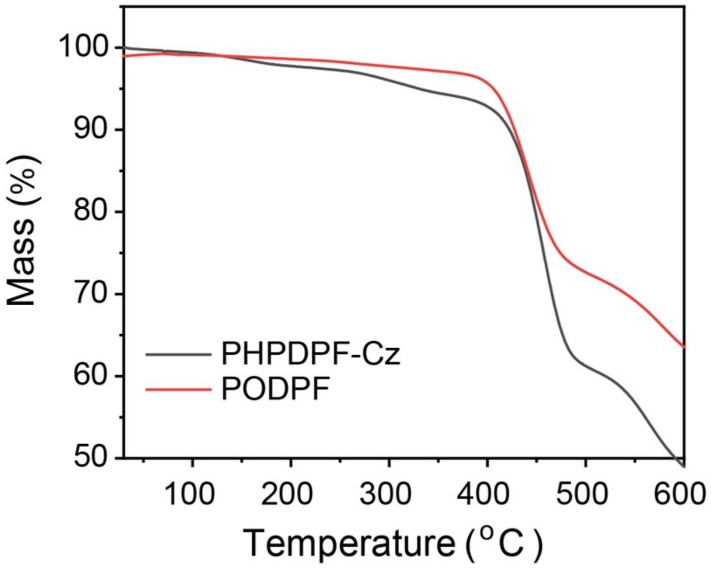


Figure S3. TGA curve of PHPDPF-Cz and PODPF.

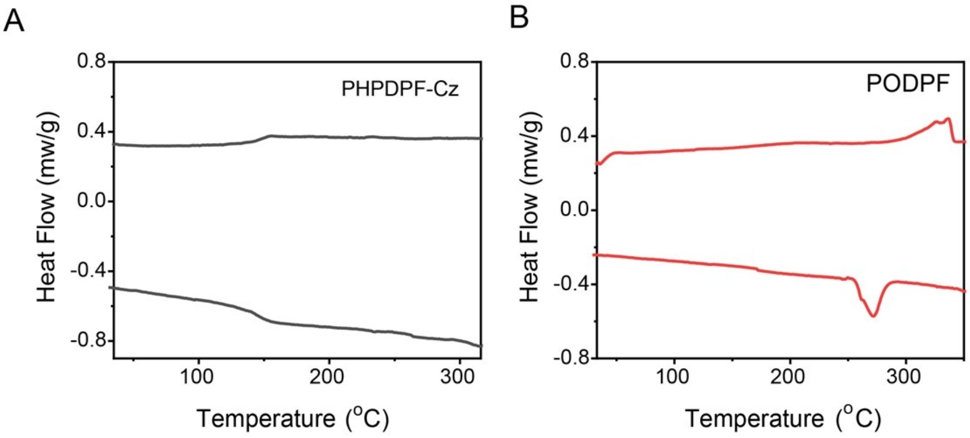


Figure S4. DSC curve of PHPDPF-Cz and PODPF.

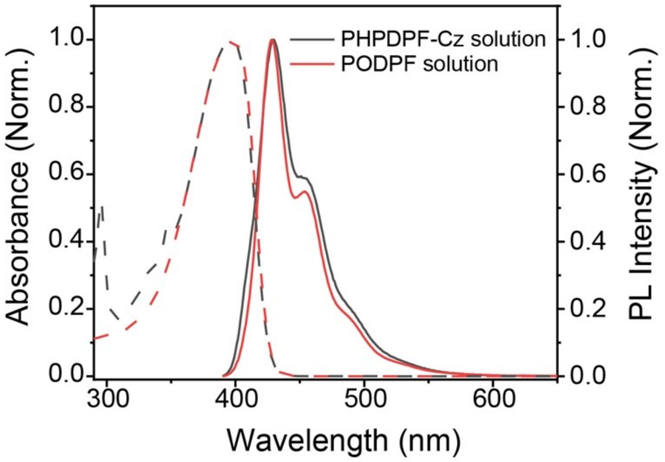


Figure S5. UV-*vis* and PL spectra of PHPDPF-Cz and PODPF for diluted chloroform solution.

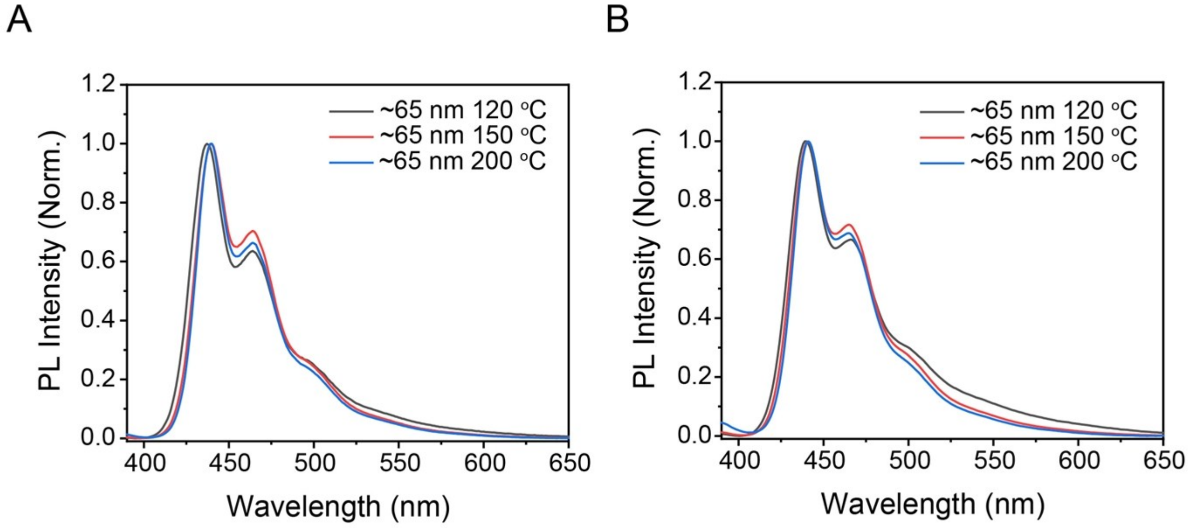


Figure S6. Normalized PL spectra of PHPDPF-Cz for annealed films which spin-coated from toluene solution (10 mg/ml). Annealed films were obtained via keeping the pristine spin-coated film after thermal annealed at 120 °C, 150 °C and 200 °C in ambient atmosphere, respectively. Thus, the left one aging for 3 days, and the right one aging for 8 days.

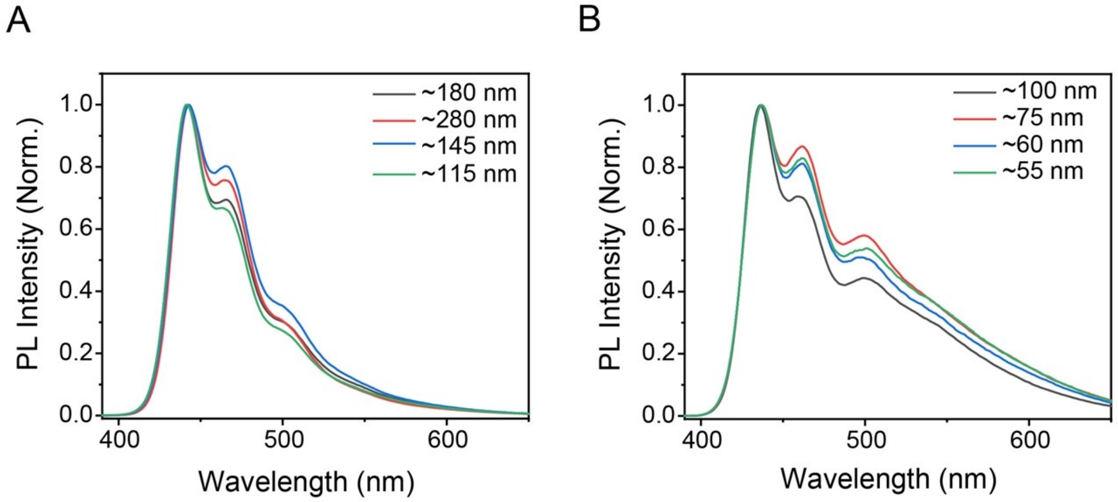


Figure S7. Normalized UV-vis and PL spectra of PHPDPF-Cz and PODPF for films which spin-coated from toluene solution under defferent speed that 500 r/min, 1000r/min, 2000r/min and 3000r/min, respectively.Then these films aged for 14 days in ambient atmosphere.

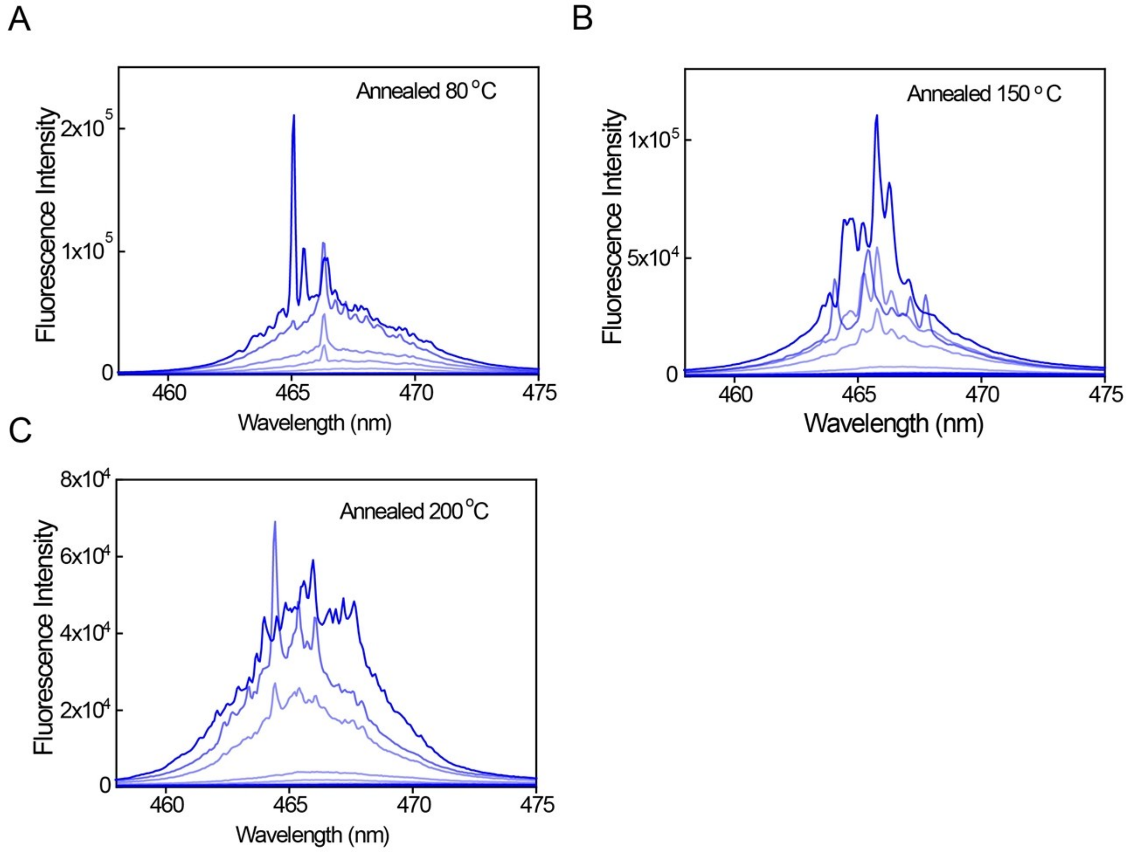


Figure S8. ASE behavious of PHPDPF-Cz for annealed films. Annealed films were obtained via keeping the pristine spin-coated film after thermal annealed at 80 ^oC, 150 ^oC and 200 ^oC in ambient atmosphere, respectively.

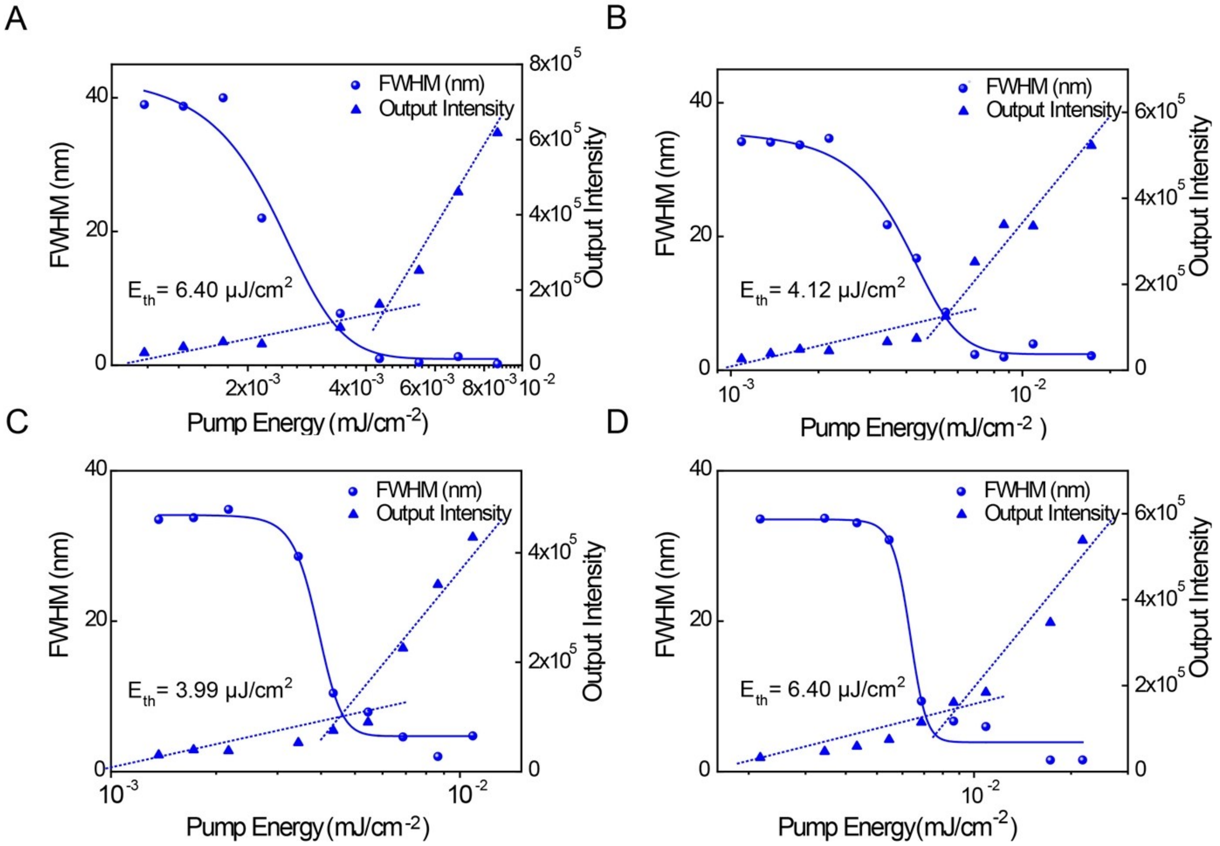


Figure S9. ASE output intensity and FWHM versus pump energy density of PHPDPF-Cz for annealed films. Annealed films were obtained via keeping the pristine spin-coated film after thermal annealed at 80 °C (A), 150 °C (B), 200 °C (C) and 220 °C (D) in ambient atmosphere, respectively.

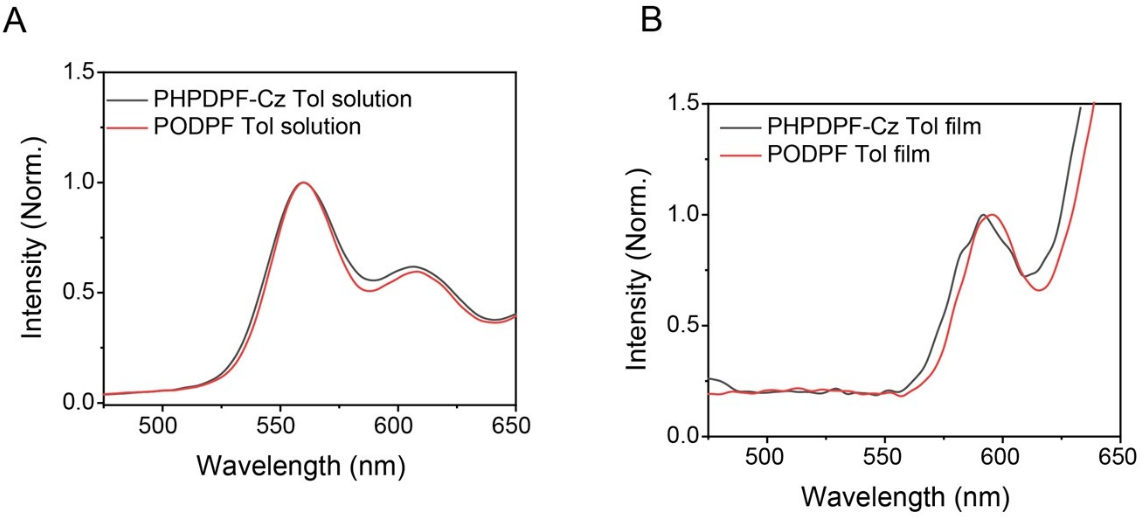


Figure S10. FL spectra of PHPDPF-Cz and PODPF for toluene solutions and films at low temperature (77K).

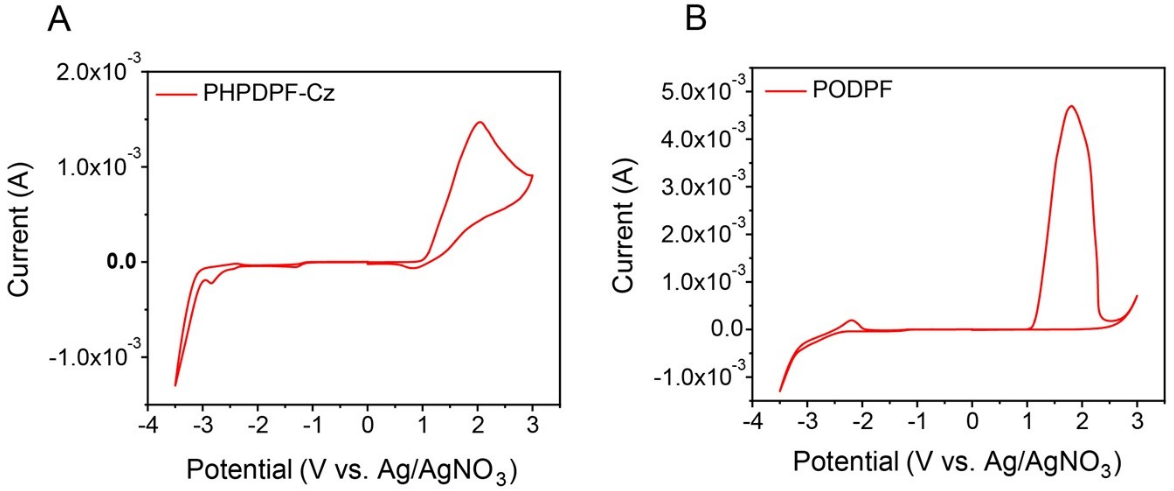


Figure S11. The CV curve of PHPDPF-Cz and PODPF.

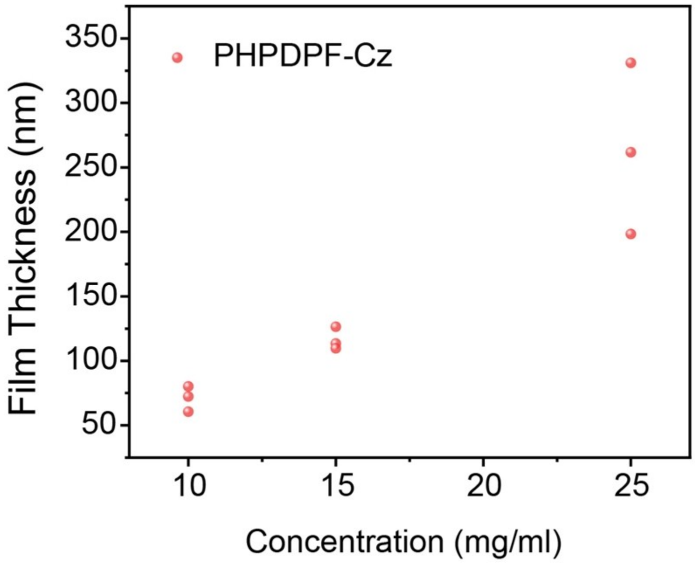


Figure S12. The film thickness of PHPDPF-Cz for films which spin-coated from toluene or solution at 10mg/ml, 15mg/ml and 25mg/ml,respectively.

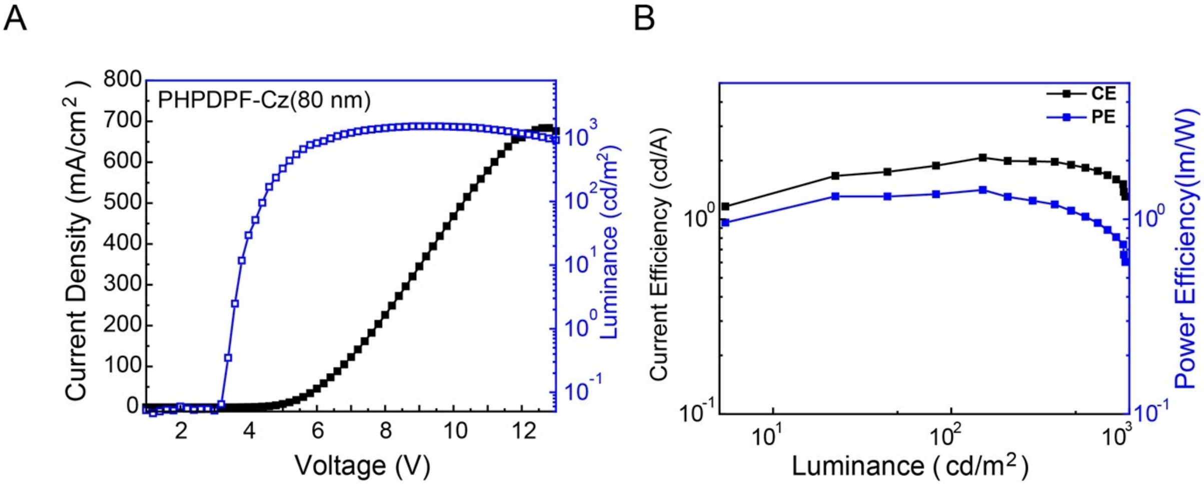


Figure S13. Performance of PLEDs based on PHPDPF-Cz with a thickness of ~80 nm.

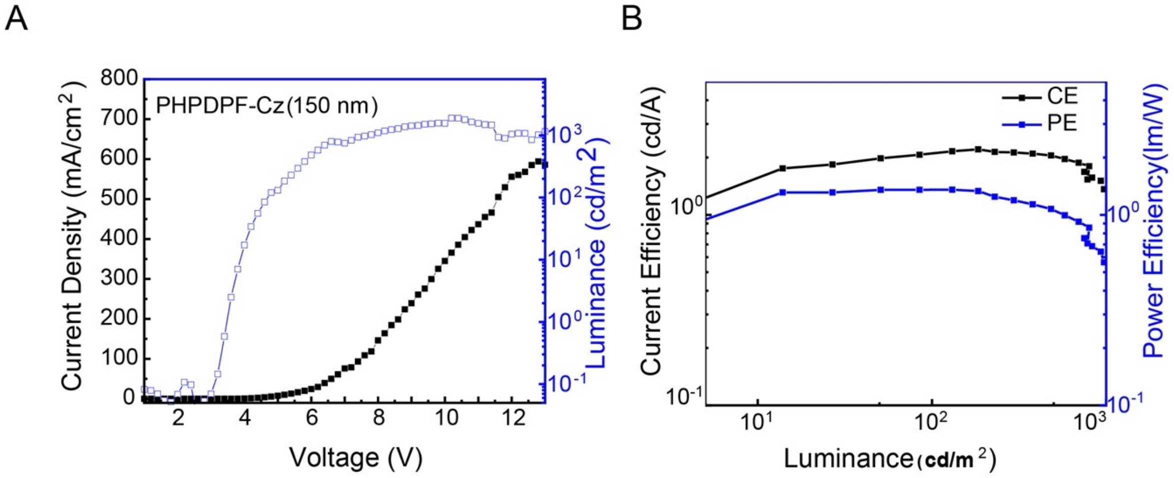


Figure S14. Performance of PLEDs based on PHPDPF-Cz with a thickness of ~150 nm.

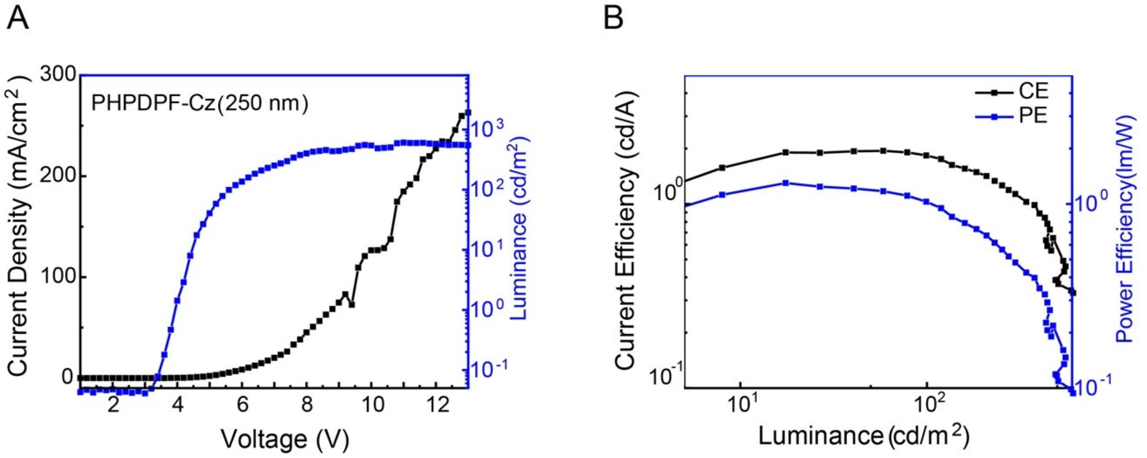
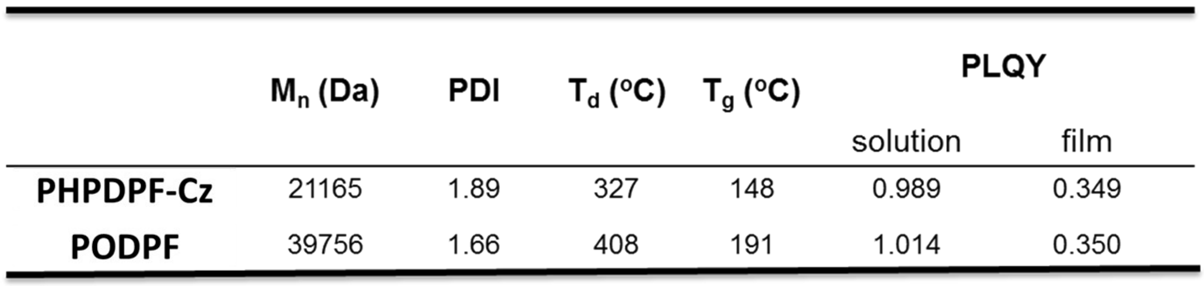


Figure S15. Performance of PLEDs based on PHPDPF-Cz with a thickness of ~250 nm.

Table S1. Summary of the structural data of the PHPDPF-Cz and PODPF.

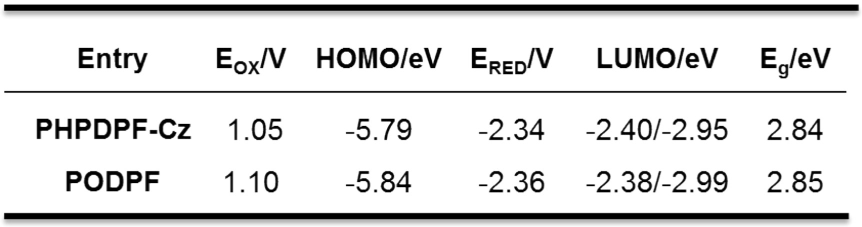


	M_n (Da)	PDI	T_d (°C)	T_g (°C)	PLQY	
					solution	film
PHPDPF-Cz	21165	1.89	327	148	0.989	0.349
PODPF	39756	1.66	408	191	1.014	0.350

Table S2. Summary of the structural data of ASE of PHPDPF-Cz for annealed films. Annealed films were obtained via keeping the pristine spin-coated film after thermal annealed at 80 ^{o}C, 150 ^{o}C, 200 ^{o}C and 220 ^{o}C in ambient atmosphere, respectively.

	E_{th}/(uJ.cm^{-2})	FWHM/(nm)	λ_{ASE}/(nm)
80 ^{o}C	2.19	0.7	466
150 ^{o}C	4.12	2.6	466
200 ^{o}C	3.99	3.8	464
220 ^{o}C	6.40	1.5	464

Table S3. Summary of the structural data of CV of PHPDPF-Cz and PODPF.



Entry	E_{OX}/V	HOMO/eV	E_{RED}/V	LUMO/eV	E_g/eV
PHPDPF-Cz	1.05	-5.79	-2.34	-2.40/-2.95	2.84
PODPF	1.10	-5.84	-2.36	-2.38/-2.99	2.85

Table S4. Summary of the structural data of PLED of PHPDPF-Cz.

Emitters	λ max	Von (V)	Lmax (cd m^{-2})	CE/PE/EQE [cd A^{-1}/lm W^{-1}/%]		
				Maximum	@100 cd m^{-2}	@1000 cd m^{-2}
50 nm	440/468	3.7	1687	2.07/1.41/1.80	1.95/1.38/1.70	1.26/0.57/1.10
150 nm	440/468	3.7	1894	2.21/1.33/1.86	2.11/1.35/1.78	1.32/0.53/1.11
250	440/468	3.7	1310	2.06/1.19/1.72	1.94/1.18/1.62	2.28/0.54/1.07