

Supporting Information

Unsymmetrical substituted steric terfluorenes for solution processed narrowband deep-blue organic light-emitting diodes with $CIE_y=0.06$

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EXPERIMENTAL SECTION

Chemicals. All reagents from commercial sources were used without further purification, unless otherwise noted. Tetrahydrofuran (THF) was deoxidized under a nitrogen atmosphere immediately prior to use. All the developed materials were purified by column chromatography.

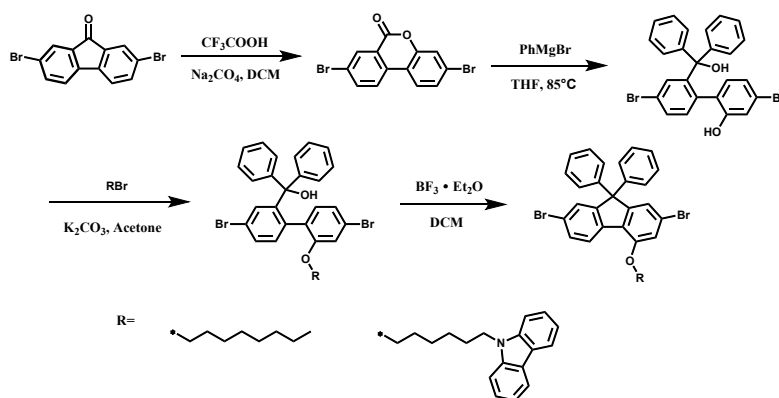
Characterization. ^1H - and ^{13}C -NMR spectrum was recorded on a JOEL NMR spectrometer (JNM-ECZ400S, 400 MHz Japan) in CDCl_3 with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GCMS 2010 PLUS. UV-visible absorption spectra were taken with a Shimadzu UV-1750 spectrometer at room temperature, and photoluminescence spectra were measured using Hitachi F-4600. Thermogravimetric analysis (TGA) was acquired by TGA2 (Mettler Instruments). Differential scanning calorimetry (DSC) data was measured by DSC214 Polyma (NETZSCH Instruments) with the measured temperature from 25°C to 310°C at a rate of $10^\circ\text{C}/\text{min}$. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M. tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) 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 energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): $\text{HOMO/LUMO} = - [\text{E}_{\text{onset}} - \text{E}_{(\text{Fc}/\text{Fc}^+)} + 4.8]$ eV, the Fc/Fc^+ redox were used as an internal standard to calibrate the oxidation potential of the materials. The film morphologies of compounds 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 measurement of PL lifetime was obtained on Edinburgh FLS980 fluorescence spectrophotometer with a xenon arc lamp (Xe900). The PLQY of polymer films were determined with a spectrometer C11347 (Hamamatsu, Japan).

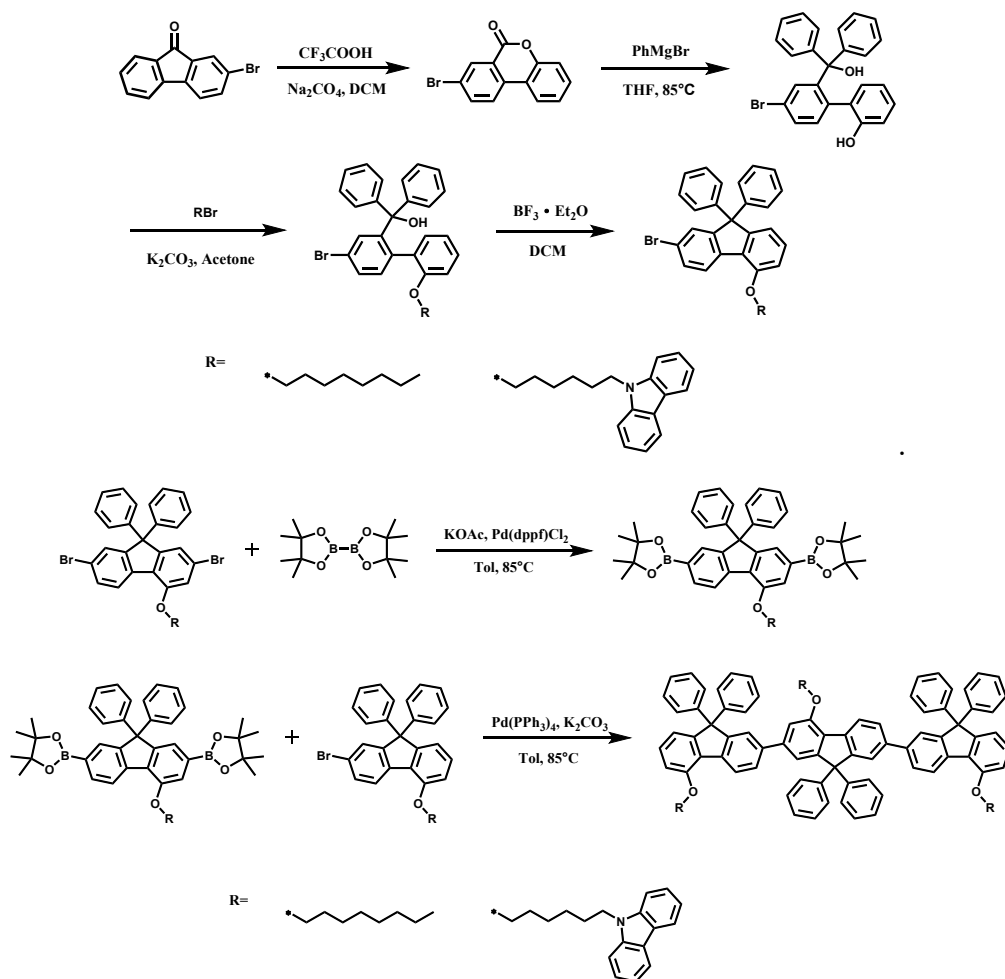
Theoretical Calculation. Density functional theory (DFT) calculations were carried out using Gaussian 03 (B3LYP nonlocal density functional with a 6-31G(d) basis set). The geometry of the ground state of the two molecules in the gas phase was optimized. For better understanding of the structure-property relationships of the developed

materials, the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital were acquired.

OLEDs Fabrication. The OLEDs structure was ITO/PEDOT:PSS/EML/TPBi/LiF/Al. Before spin-coating, the ITO substrate was cleaned in an ultrasonic bath with detergent, acetone, isopropanol and deionized water, dried in an oven at 120°C for 2 hours, and treated with ultraviolet ozone for 10 min. Firstly, a 40 nm thick PEDOT:PSS was spin-coated with a speed of 1500 r/min (30 s) and then annealed at 120°C for 15 minutes. Then, the emitting layer was spin-coated from CB solution (10 mg/mL) with a speed of 1500 r/min (30 s) and annealed at 120°C for 15 minutes in nitrogen-filled glovebox. And the thickness of P8 spin-coated film is estimated about 40 nm. Finally, the residue layers, such as 25 nm TPBi, 0.8 nm LiF, and 100 nm Al, were deposited by thermal evaporating at a pressure below 1×10^{-5} mbar. The area of the device was 4 mm² defined by the overlap between the ITO and Al electrode. The EL spectra were measured using a QE65 Pro (Ocean Optics) spectrometer in air with encapsulated devices.

Materials synthesis.





Scheme S1. The specific steps of material synthesis.

2-bromo-5-(octyloxy)-9,9-diphenyl-9H-fluorene (ODPF-Br).

The 4'-bromo-2'-(hydroxydiphenylmethyl)-[1,1'-biphenyl]-2-ol (0.50 g, 1.16 mmol) and 1-bromooctane (0.22 g, 1.16 mmol) was dissolved in anhydrous acetone (20 mL). After K_2CO_3 (0.32 g, 2.32 mmol) was dropped in the flask and kept the reaction stirred for 24 h. Then the mixture was separated by suction filtration using Buchner funnel and washed by dichloromethane for several times. The dichloromethane organic layer was washed by dichloromethane for several times. The dichloromethane organic layer was dehydrated with dried over Na_2SO_4 . After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford intermediate products. A solution of boron trifluoride–diethyl ether complex (0.20 mL) in appropriate dichloromethane (10 mL) was added dropwise to a solution of intermediate products 0.63 g (1.16 mmol). The reaction mixture was stirred at 25°C for 6 h. Ethanol and water 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 (Na_2SO_4). The residue was purified by column chromatography on silica gel to afford ODPF-Br (yield 94%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.53 (s, 2H), 7.22 (s, 11H), 7.02 (s, 1H), 6.89 (s, 1H), 4.18 (s, 2H), 2.00 (s, 2H), 1.59 (s, 2H), 1.36 (s, 8H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.41 , 152.82 , 152.71 , 145.29 , 138.68 , 130.64 , 129.17 , 128.74 , 128.34 , 128.18 , 126.99 , 126.85 , 125.39 , 120.44 , 118.10 , 110.03 , 68.15 , 65.74 , 31.87 , 29.43 , 29.31 , 26.30 , 22.74 , 14.21.

9-((7-bromo-9,9-diphenyl-9H-fluoren-4-yl)oxy)hexyl)-9H-carbazole (HDPF-Br).

The 4'-bromo-2'-(hydroxydiphenylmethyl)-[1,1'-biphenyl]-2-ol (0.50 g, 1.16 mmol) and 9-(6-bromohexyl)-9H-carbazole (0.38 g, 1.16 mmol) was dissolved in anhydrous acetone (20 mL). After K_2CO_3 (0.32 g, 2.32 mmol) was dropped in the flask and kept the reaction stirred for 24 h. Then the mixture was separated by suction filtration using Buchner funnel and washed by dichloromethane for several times. The dichloromethane organic layer was dehydrated with dried over Na_2SO_4 . After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford intermediate products. A solution of boron trifluoride–diethyl ether complex (0.20mL) in appropriate dichloromethane (10 mL) was added dropwise to a solution of intermediate products 0.79 g (1.16 mmol). The reaction mixture was stirred at 25 °C for 6 h. Ethanol and water 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 (Na_2SO_4). The residue was purified by column chromatography on silica gel to afford HDPF-Br (yield 94%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 2H), 7.95 (s, 1H), 7.43 (s, 6H), 7.21 (s, 13H), 6.97 (s, 1H), 6.81 (s, 1H), 4.35 (s, 2H), 4.09 (s, 2H), 1.95 (s, 4H), 1.62 (s, 2H), 1.52 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.32, 145.32, 140.50, 138.66, 130.72, 129.24, 128.85, 128.41, 128.24, 126.93, 125.74,

125.34, 122.91, 120.49, 118.88, 118.27, 110.09, 108.71, 67.89, 43.03, 29.32, 29.12, 27.19, 26.25, 1.13.

4',5,5''-tris(octyloxy)-9,9,9',9',9'',9''-hexaphenyl-9H,9'H,9''H-2,2':7',2''-terfluorene (MC8).

2,2'-(4-(octyloxy)-9,9-diphenyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.50 g, 0.72 mmol), 2-bromo-5-(octyloxy)-9,9-diphenyl-9H-fluorene (0.94 g, 1.79 mmol), and tetrakis(triphenylphosphine)palladium (0) (0.09 g, 0.08 mmol) were added into toluene (15 mL), After adding 2 mol L⁻¹ aqueous solution of K₂CO₃ (3 mL) to the mixture, the mixture was stirred at 85°C for 24 h under a nitrogen atmosphere. Then the mixture was separated by suction filtration using Buchner funnel and washed by dichloromethane for several times. The dichloromethane organic layer was dehydrated with dried over Na₂SO₄. After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford MC8 (yield 80%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 3H), 7.55 (s, 6H), 7.21 (s, 33H), 6.99 (s, 3H), 6.85 (s, 2H), 4.15 (s, 6H), 1.97 (s, 6H), 1.29 (d, *J* = 25.2 Hz, 30H), 0.89 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.54, 155.50, 153.65, 153.35, 153.30, 151.50, 151.27, 151.18, 146.14, 142.39, 140.12, 139.93, 139.87, 139.09, 138.81, 128.76, 128.42, 128.40, 128.37, 128.32, 127.90, 127.79, 126.90, 126.71, 124.29, 118.29, 117.25, 110.01, 109.35, 68.18, 65.95, 65.85, 31.97, 29.57, 29.52, 29.38, 26.39, 22.83, 14.30, 1.17.

9,9',9''-(((9,9,9',9',9'',9''-hexaphenyl-9H,9'H,9''H-[2,2':7',2''-terfluorene]-4',5,5''-triyloxy)tris(hexane-6,1-diyl)tris(9H-carbazole) (MC6Cz).

9-(6-((9,9-diphenyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-4-yl)oxy)hexyl)-9H-carbazole (0.50 g, 0.60 mmol), 9-(6-((7-bromo-9,9-diphenyl-9H-fluorene-4-yl)oxy)hexyl)-9H-carbazole (0.99 g, 1.50 mmol), and tetrakis(triphenylphosphine)palladium (0) (0.09 g, 0.08 mmol) were added into toluene (15 mL), After adding 2 mol L⁻¹ aqueous solution of K₂CO₃ (3 mL) to the mixture, the mixture was stirred at 85°C for 24 h under a nitrogen atmosphere. Then the mixture was

separated by suction filtration using Buchner funnel and washed by dichloromethane for several times. The dichloromethane organic layer was dehydrated with dried over Na_2SO_4 . After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford MC6Cz (yield 80%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 9H), 7.53 (s, 6H), 7.43 (s, 12H), 7.21 (s, 39H), 7.00 (d, $J = 7.6$ Hz, 2H), 6.95 (s, 1H), 6.81 (d, $J = 8.2$ Hz, 2H), 4.34 (s, 6H), 4.11 (s, 6H), 1.95 (s, 12H), 1.65 (s, 6H), 1.53 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.41, 153.70, 153.40, 151.22, 146.11, 142.40, 140.55, 140.15, 139.89, 139.09, 138.47, 128.72, 128.39, 128.35, 127.88, 127.77, 126.96, 126.76, 125.77, 124.23, 124.10, 122.95, 120.50, 118.90, 118.42, 117.36, 110.04, 108.79, 67.89, 65.96, 65.87, 43.07, 29.86, 29.43, 29.13, 27.22, 26.30, 1.19.

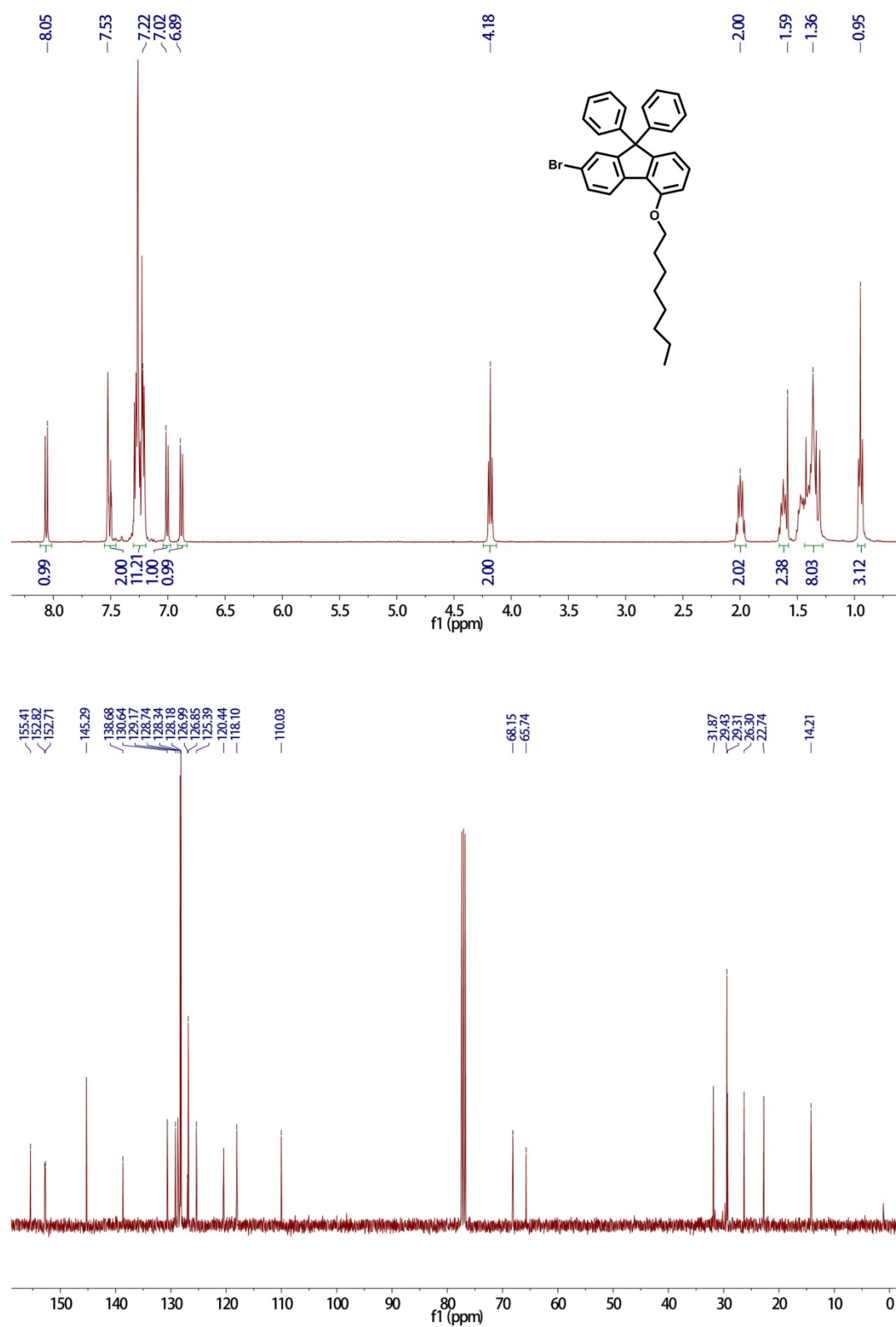


Figure S1. ^1H and ^{13}C NMR spectra of ODPF-Br in CDCl_3 .

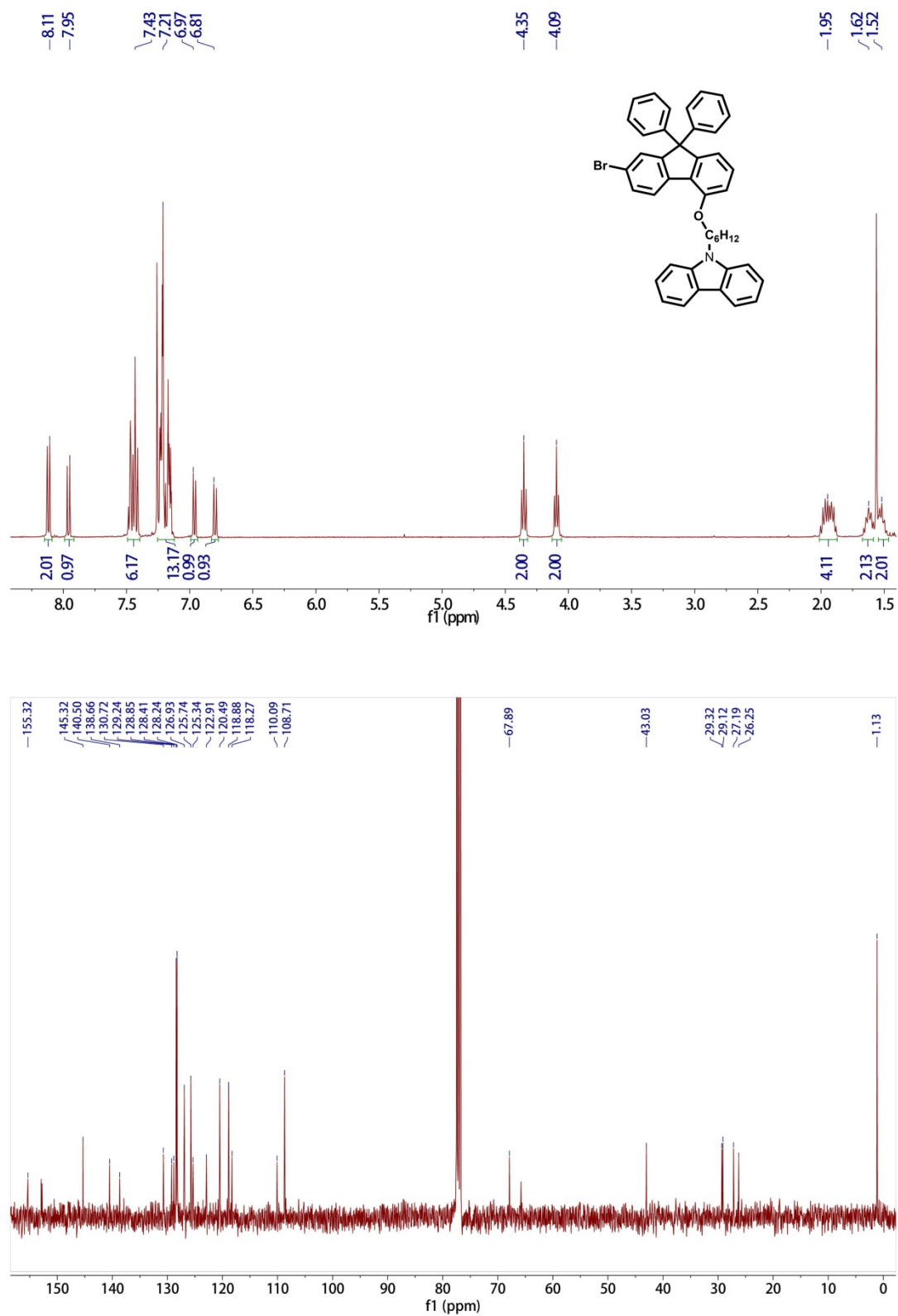


Figure S2. ^1H and ^{13}C NMR spectra of HDPF-Br in CDCl_3 .

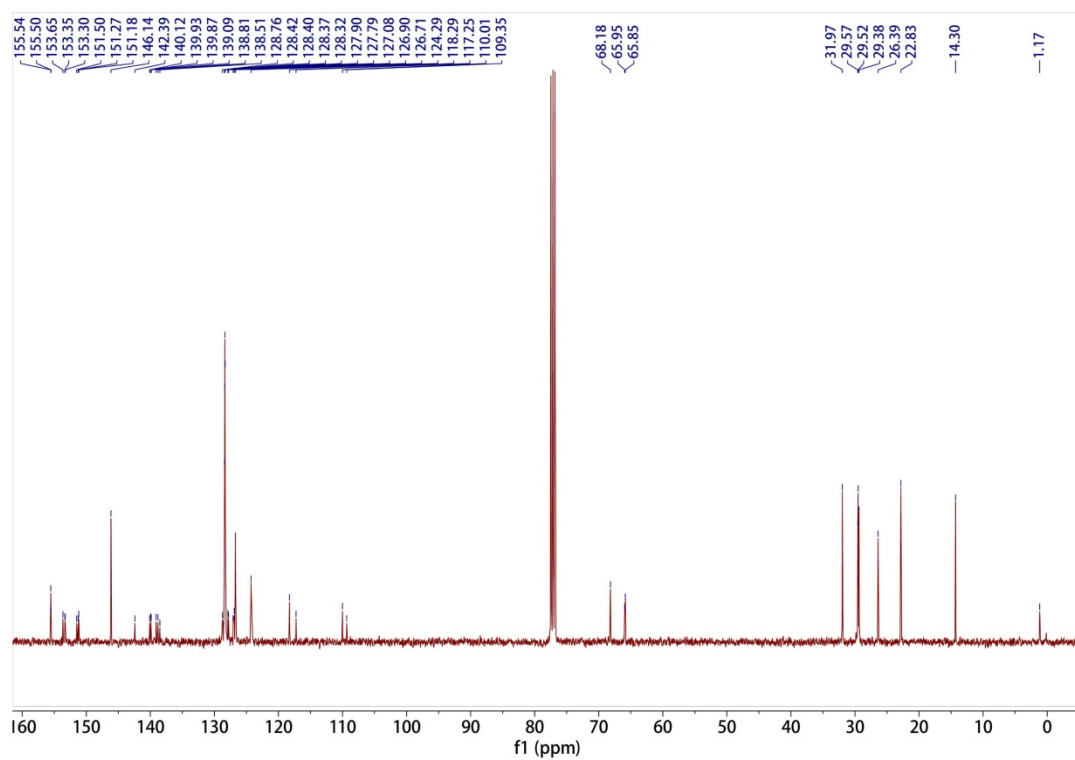
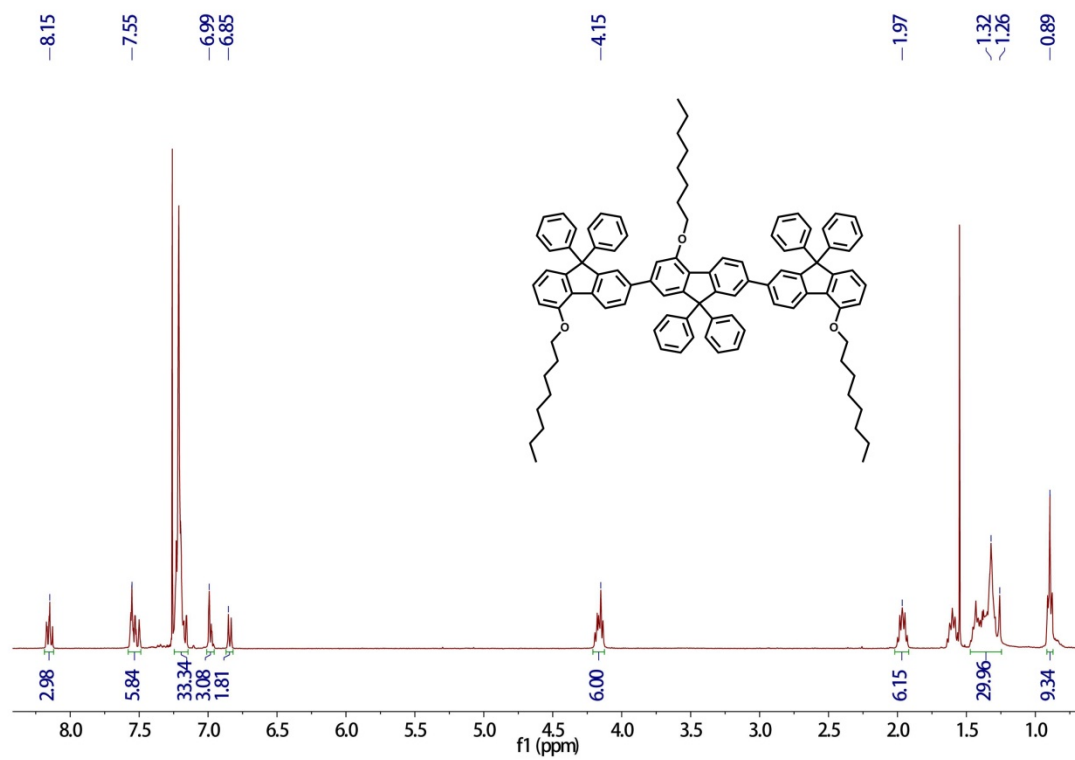


Figure S3. ¹H and ¹³C NMR spectra of MC8 in CDCl₃.

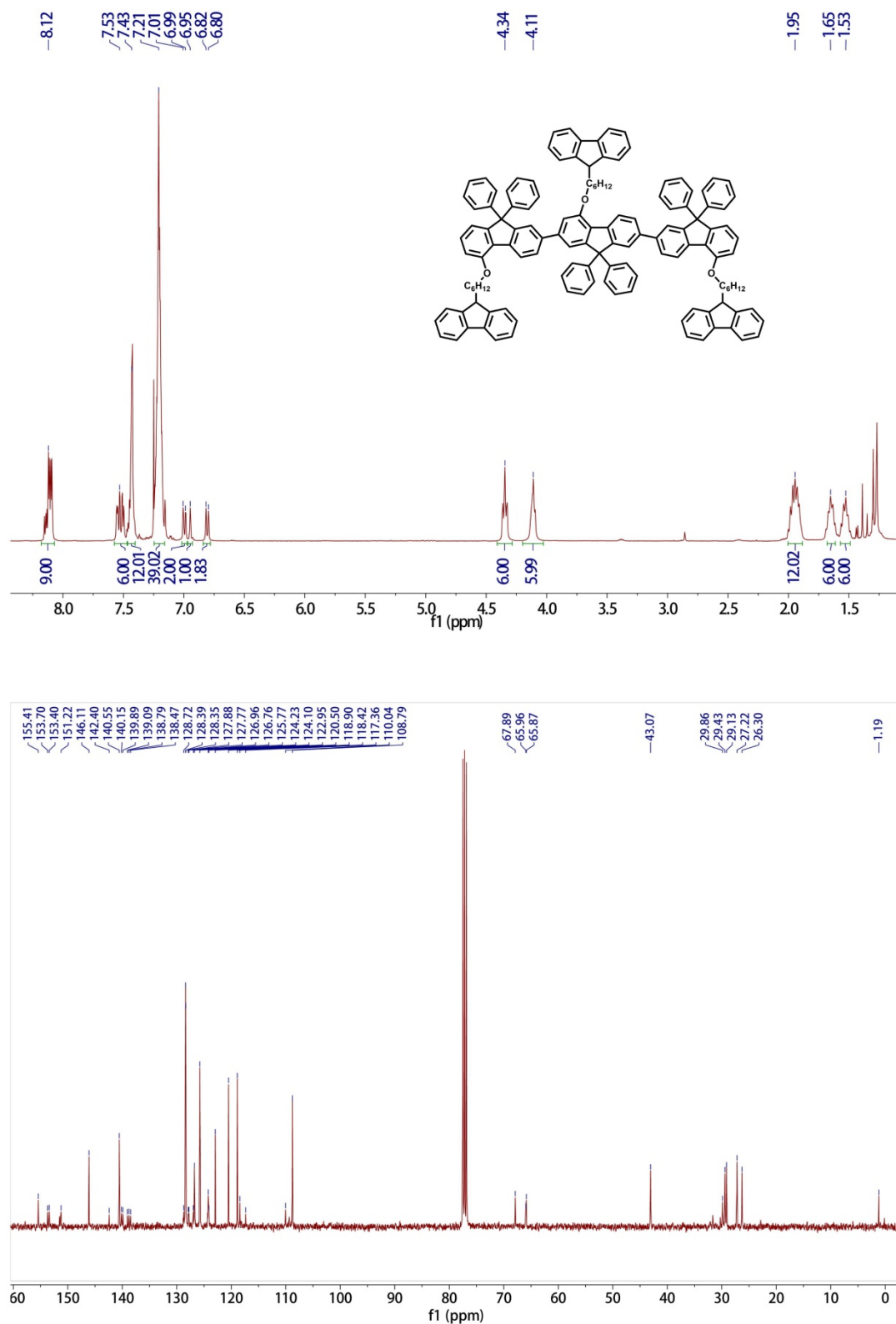


Figure S4. ^1H and ^{13}C NMR spectra of MC6Cz in CDCl_3 .

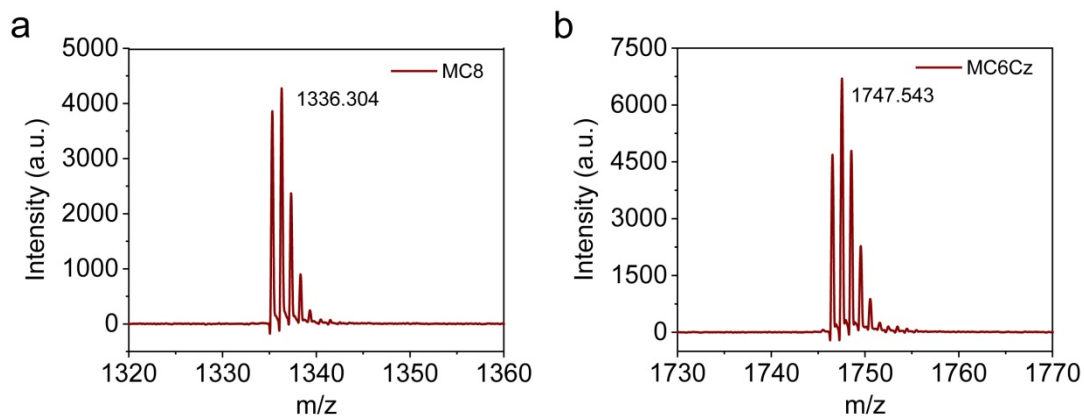


Figure S5. Mass curves of (a) MC8 and (b) MC6Cz for solid powder.

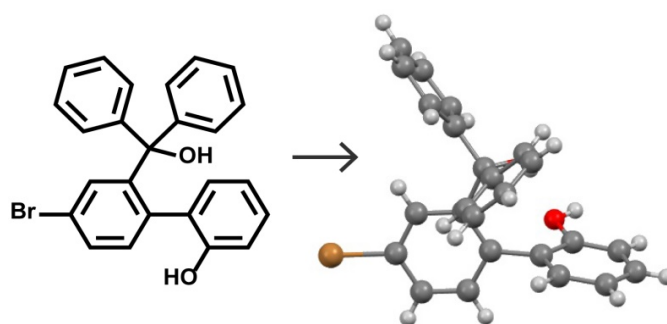


Figure S6. Single crystal structure of the material.

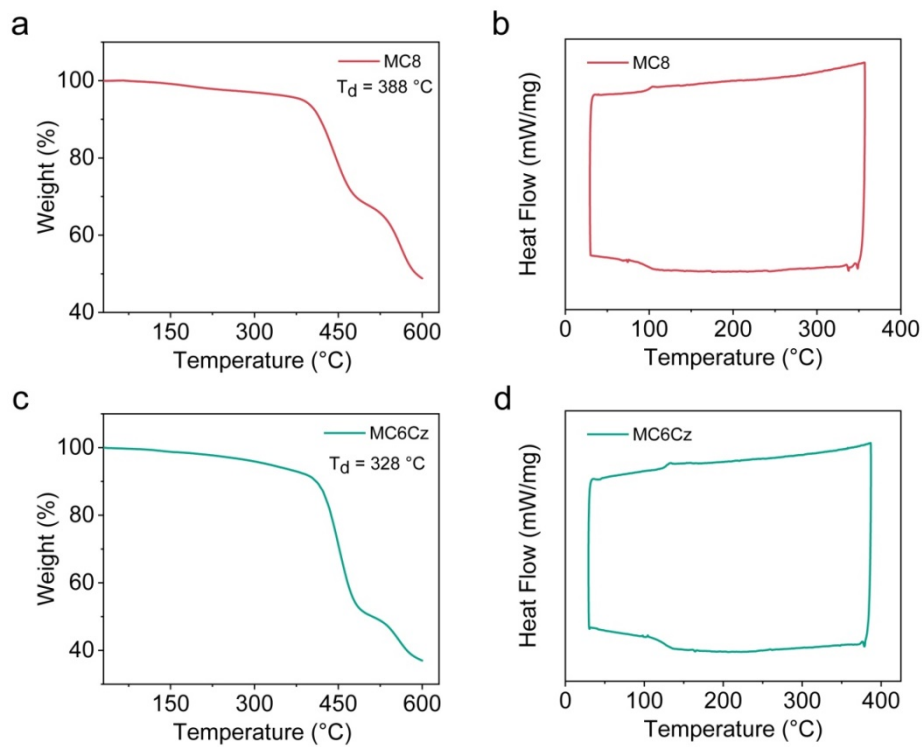


Figure S7. TGA curves of (a) MC8 and (c) MC6Cz. DSC curves of (b) MC8 and (d) MC6Cz. Heating rate was 10 K/min under nitrogen atmosphere.

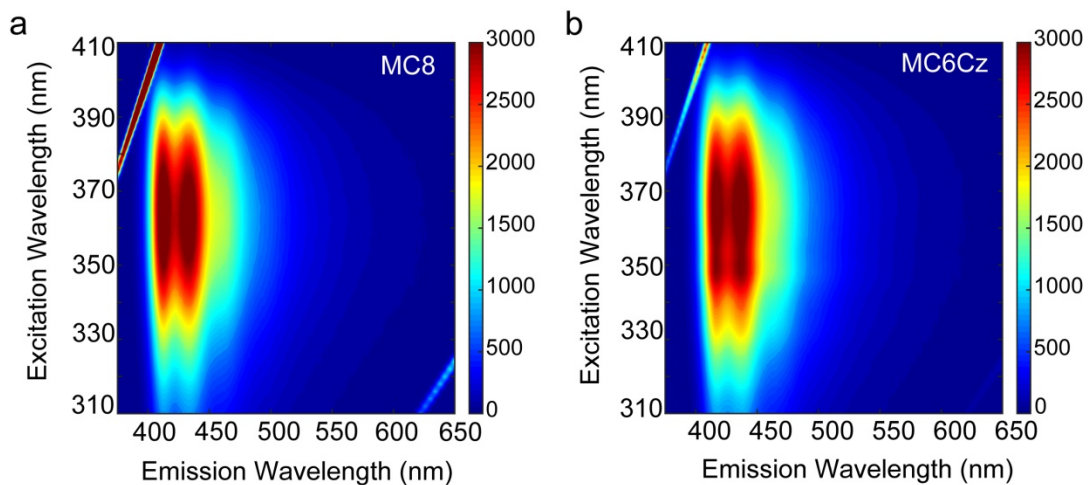


Figure S8. PL spectral mapping images of (a) MC8 and (b) MC6Cz for spin coating films.

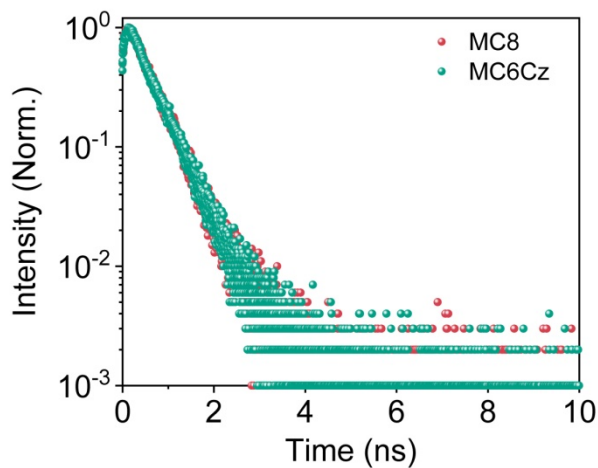


Figure S9. Time-resolved fluorescence decays spectra of MC8 and MC6Cz spin-coated films.

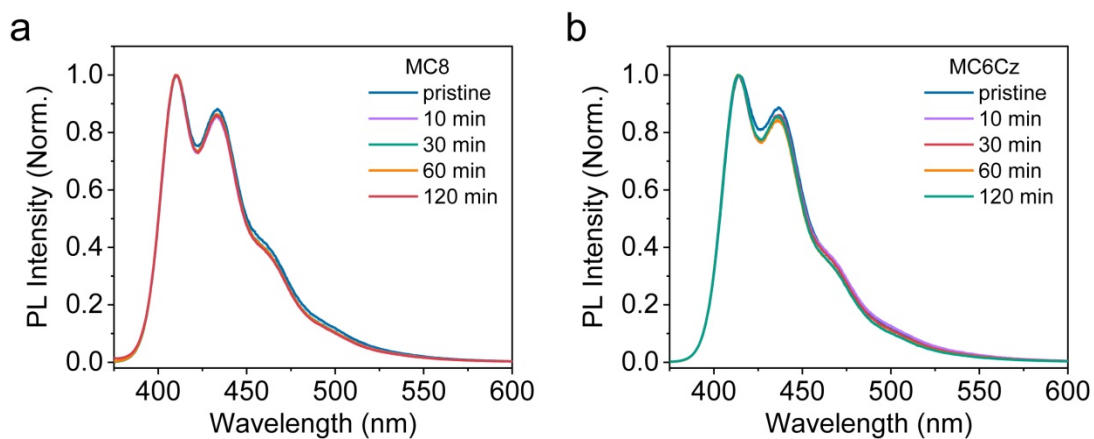


Figure S10. PL spectra of (a) MC8 and (b) MC6Cz films obtained after thermal annealed under 120°C for different times.

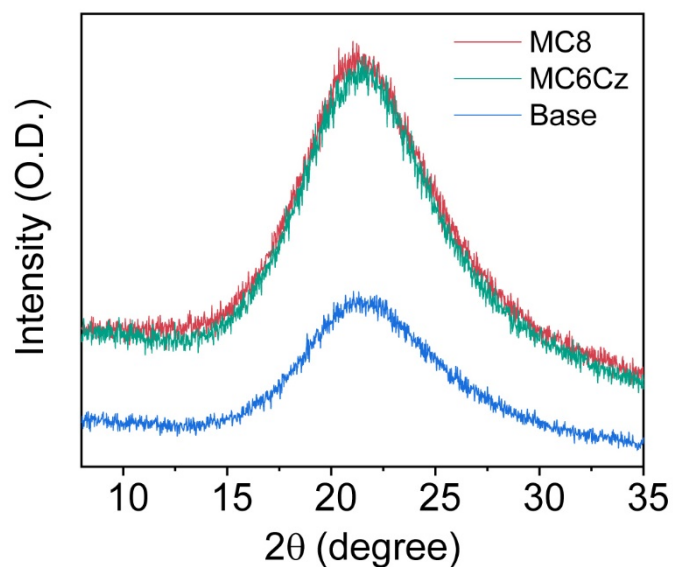


Figure S11. The XRD curves of MC8 and MC6Cz in thin solid films spin-coated with toluene solution on quartz substrate.

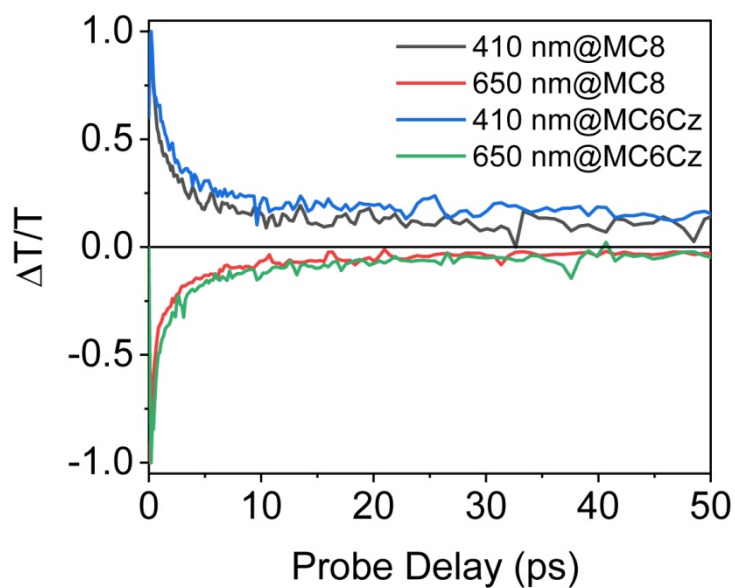


Figure S12. The SE time-decay dynamics at 410 nm and the PA dynamics tracing of two spin-coated films at 650 nm.

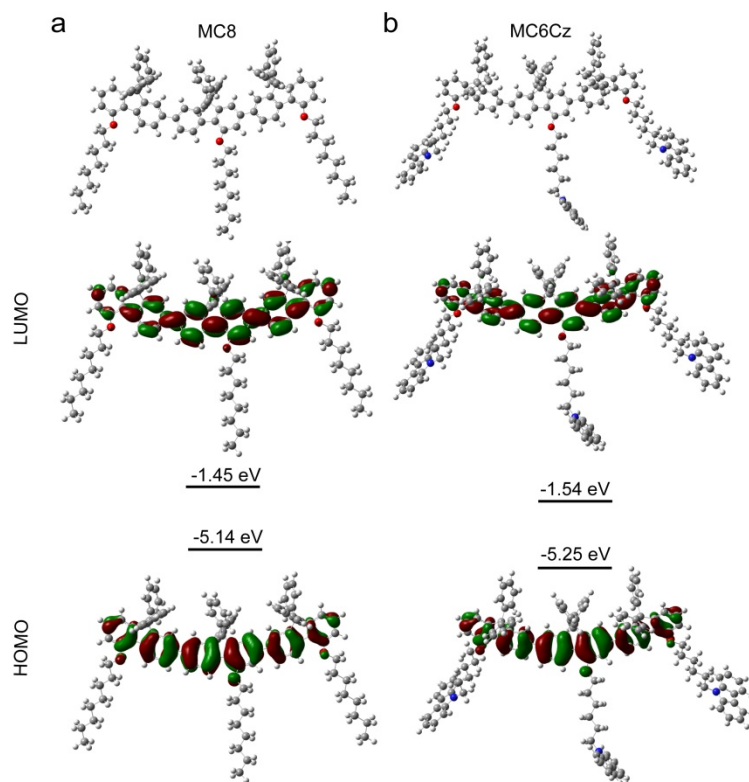


Figure S13. Geometrically optimized structure of (a) MC8 and (b) MC6Cz, calculated LUMO and HOMO electronic wavefunction distributions.

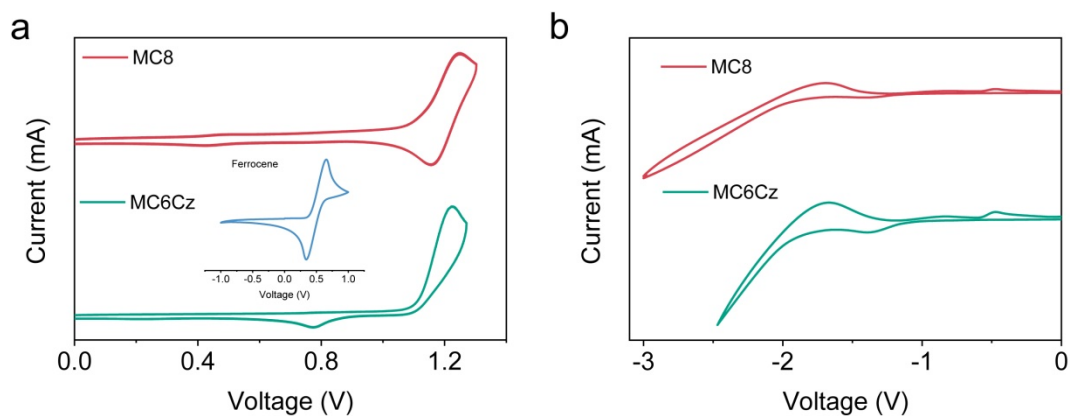


Figure S14. Cyclic voltammograms curves of MC8 and MC6Cz. (a) Oxidation potential. (b) Reduction potential.