

Supporting Information

Solution-Processed Diarylfluorene Derivatives for Violet-Blue Amplified Spontaneous Emission and Electroluminescence

Ya-Min Han,^{a,†} Lu-Bing Bai,^{a,†} Chang-Jin Ou,^a Xin-Wen Zhang,^b Zong-Yan Zuo,^b Bin Liu,^b Meng-
Na Yu,^b Jin-Yi Lin,^{a*} Cheng-Rong Yin,^a Jian-Feng Zhao,^a Wen-Sai Zhu,^a Yu-Yu Liu,^b Jie-Wei
Li,^{a*} Jian-Pu Wang,^a Ling-Hai Xie,^b Wei Huang^{a,b,c*}

^aKey Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM),
Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech
University (NanjingTech), 30 South Puzhu Road, Nanjing, China *Email: iamjylin@njtech.edu.cn,
iamjwli@njtech.edu.cn, wei-huang@njtech.edu.cn

^bKey Laboratory for Organic Electronics and Information Displays & Institute of Advanced
Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials
(SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing, China

^cShaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical University (NPU),
127 West Youyi Road, Xi'an 710072, Shaanxi, China

EXPERIMENTAL SECTION

Chemicals. All starting materials and solvents were purchased from Adamas, Sigma-Aldrich and Alfa Aesar, and used as received without further purification. Tetrahydrofuran (THF) was deoxidized under a nitrogen atmosphere immediately prior to use. MC₆Cz and MC₈ were synthesized according to literature procedures.¹ Synthetic methods of the MC₆Cz and MC₈ cores derived compounds are outlined in the following. All the developed materials were purified by column chromatography.

Characterization. ¹H- and ¹³C-NMR were recorded on a Bruker 400 MHz spectromet spectrometer in CDCl₃ with tetramethylsilane (TMS) as the interval standard. Thermogravimetric analyses (TGA) measurements were conducted by a Shimadzu DTG-60H under a heating rate of 10 °C/min and a nitrogen flow rate of 50 cm³/min. DSC measurements were performed using a Shimadzu Instruments DSC-60A and DSC data were collected from 50 to 250 °C at a rate of 10 °C /min under N₂ flow. Cyclic voltammetric (CV) studies were conducted on a CHI660C Electrochemical Workstation 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-Bu₄NPF₆) in acetonitrile at a sweeping rate of 50 mV/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): HOMO/ LUMO = -[E_{onset} - E(Fc/Fc⁺) + 4.8] eV, the Fc/Fc⁺ redox were used as an internal standard to calibrate the oxidation potential of the materials. The AFM images of the 6 compounds' films spin-coated on quartz substrates were obtained by using a Dimension 3100 (Veeco, CA) in tapping model with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N m⁻¹) at a scanning rate of 1 Hz. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at room temperature, and emission spectra were recorded on a Hitachi F-4600 luminescence spectrometer. The low temperature emission spectra were recorded on a Hitachi F-4600 luminescence spectrometer, and the film samples were added into a quartz tube and dipped into a quartz container filled with liquid nitrogen. The transient PL was measured using a Coherent mode-locked Ti: Sapphire laser system with the wavelength of 390 nm and 150 fs laser pulses to excite the samples. Emission from the samples was collected at a back scattering angle of 150° by a pair of lenses and directed to an OptronisOptoscope™ streak camera, with a temporal resolution of 6 ps.

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 six 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.

Preparation of the 6 Compounds Solutions and Films. The preparation of the solutions was carried out by dissolving the compounds in the organic solvents spontaneously overnight. Pristine films of compounds for UV-PL spectra, AFM and ASE analysis, were spin-coated on quartz substrates from their toluene solutions (10mg/ml) using KW-4A (from the institute of micro-electronics of Chinese Academy of Science) at 2000 rpm for 30s. Low temperature for PL spectra is about 77 K.

Device Fabrication and Characterization. The OLED devices were fabricated onto prepatterned indium-tin oxide (ITO) whose sheet resistance is 10 Ω per square. The substrates were thoroughly cleaned in ultrasonic bath with detergent, ethyl alcohol, acetone, and demineralized water, then dried in an oven for 120 min, and finally treated in an ultraviolet-ozone chamber. A thin hole-injection layer (40 nm) of precoated poly(ethylenedioxythiophene)/polystyrene sulfonate (PEDOT:PSS) was cast onto the ITO-coated glass substrates at a spin speed of 3000 rpm for 60 s. After baking at 120 °C for 20 min in an oven, the compounds dissolved in toluene were spin-coated on the film of PEDOT:PSS at a speed of 1500 rpm/s. The thickness of the emission layer is about 45 nm and the solutions were prepared from 10 mg/ml toluene solutions. Finally, 30 nm electron transport layer (TPBI), 1 nm LiF and 100 nm Al were deposited onto the active polymer layer successively by thermal evaporation in vacuum. The EL spectra and CIE coordinates of the devices were recorded by a spectra-scan PR655 spectrophotometer. The emission area of the devices is 12 mm². The current-voltage luminescence characteristics were measured using a combination of a Keithley source meter (model 2602) and a luminance meter. All the devices were characterized without encapsulation, and all the measurements were carried out in the ambient condition at room temperature (RT).

ASE Characterization. For investigating the optical gain properties, planar waveguides were fabricated by spin-coating the 6 compounds' films from 10 mg/ml toluene solutions and excited with a Q-switched, neodymium ion doped yttrium aluminum garnate [Nd³⁺:YAG] laser pumped optical parametric amplifier (Spectron SL450), 10 Hz, 4.2 ns pulsed excitation. The pump wavelength was chosen to match the absorption maximum of the compounds. The spot dimensions for ASE measurement was about 0.4 mm \times 4 mm.

Synthesis

4-(7-(4-(diphenylamino)phenyl)-5-(hexyl carbazole)-9,9-diphenyl-9H-fluorene-2-yl)-N,N-diphenylbenzidine (MC₆Cz-TPA). 4-(diphenylamino)phenylboronic acid (0.8 g, 2.7 mmol) and MC₆Cz (0.57 g, 0.8 mmol) were dissolved in a mixed solvent of THF/distilled water (25 ml). To the mixture, 1.4 g potassium carbonate aqueous solution (5 ml) and tetrakis(triphenylphosphine)palladium(0) (0.1 g) were added slowly and refluxed 36 h under a nitrogen atmosphere. The mixture was extracted with distilled water and dichloromethane after cooling the reaction mixture to room temperature. 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 MC₆Cz-TPA (0.45 g, yield 53%). ¹H NMR (400 MHz, Chloroform-d) δ : 8.18 – 8.05 (m, 3H), 7.59 – 7.51 (m, 2H), 7.49 – 7.38 (m, 8H), 7.32 – 7.26 (m, 9H), 7.25 – 7.18 (m, 12H), 7.11 (t, 12H), 7.06 – 7.00 (m, 5H), 4.36 (t, J = 7.1 Hz, 2H), 4.19 (t, J = 6.3 Hz, 2H), 2.03 – 1.94 (m, 4H), 1.74 – 1.63 (m, 2H), 1.34 – 1.25 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.34, 153.78, 151.57, 147.70, 147.65, 147.27, 147.02, 146.02, 141.43, 140.46, 138.96, 138.18, 135.45, 135.38, 129.31, 129.29, 128.39, 128.27, 127.93, 127.76, 126.79, 126.62, 126.10, 125.68, 124.42, 124.37, 123.97, 123.82, 123.00, 122.90, 122.87, 120.40, 118.81, 116.86, 108.79, 108.67, 67.88, 65.90, 42.99, 29.75, 29.36, 29.08, 27.14, 26.22, 1.08.

9-(4-(7-(4-(9H-carbazol-9-yl)phenyl)-4-(hexylcarbazole)-9,9-diphenyl-9H-fluorene-2-yl)phenyl)-9H-carbazole (MC₆Cz-9-NPC). MC₆Cz-9-NPC (0.48 g, yield 56.2%) was synthesized in a similar manner with b instead of a (scheme 1). ¹H NMR (400 MHz, Chloroform-d) δ : 8.30 (d, 1H), 8.22 – 8.11 (m, 6H), 7.84 – 7.78 (m, 4H), 7.77 – 7.69 (m, 2H), 7.67 – 7.59 (m, 4H), 7.52 –

7.42 (m, 12H), 7.42 – 7.37 (m, 5H), 7.37 – 7.29 (m, 9H), 7.28 – 7.23 (m, 3H), 7.19 (d, J = 1.3 Hz, 1H), 4.42 (t, J = 7.1 Hz, 2H), 4.31 (t, J = 6.3 Hz, 2H), 2.13 – 2.01 (m, 4H), 1.68 – 1.58 (m, 2H), 1.32 – 1.26 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.69, 154.23, 152.01, 145.90, 141.36, 140.92, 140.90, 140.57, 140.53, 140.43, 138.90, 137.01, 136.77, 128.76, 128.57, 128.53, 128.46, 127.44, 127.32, 126.94, 126.81, 126.08, 125.76, 124.48, 124.41, 123.54, 123.52, 122.95, 120.51, 120.47, 120.43, 120.13, 120.07, 118.91, 117.39, 109.95, 109.90, 109.38, 108.74, 68.12, 66.15, 43.05, 29.83, 29.45, 29.17, 27.24, 26.33, 1.17.

2-(4-(octyloxy)-9,9-diphenyl-7-(9-phenyl-9H-carbazol-2-yl)-9H-fluoren-2-yl)-9-phenyl-9H-carbazole (MC₆Cz-2-NPC). MC₆Cz-2-NPC (0.44 g, yield 51.6%) was synthesized in a similar manner with c instead of a (scheme 1). ¹H NMR (400 MHz, Chloroform-d) δ: 8.23 – 8.09 (m, 6H), 7.69 (d, J = 1.6 Hz, 2H), 7.67 – 7.40 (m, 23H), 7.37 – 7.27 (m, 6H), 7.28 – 7.18 (m, 8H), 7.08 (d, J = 1.2 Hz, 2H), 4.42 – 4.33 (m, 2H), 4.21 (s, 2H), 1.98 (d, J = 7.3 Hz, 4H), 1.81 – 1.63 (m, 2H), 1.52 – 1.40 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.50, 153.80, 151.58, 146.20, 143.10, 141.51, 141.39, 140.56, 140.05, 139.83, 138.57, 137.72, 130.03, 128.51, 128.42, 127.60, 127.27, 127.21, 127.14, 127.12, 126.80, 126.17, 126.07, 125.78, 124.97, 124.22, 123.32, 123.29, 122.97, 122.84, 122.61, 120.62, 120.50, 120.30, 120.22, 120.04, 119.84, 118.92, 118.06, 109.97, 109.92, 108.79, 108.54, 108.38, 68.06, 66.09, 43.04, 29.90, 29.45, 29.13, 27.23, 26.32, 25.04, 1.25.

4-(7-(4-(diphenylamino)phenyl)-5-(hexylcarbazole)-9,9-diphenyl-9H-fluoren-2-yl)-N,N-diphenylbenzenimine (MC₈-TPA). MC₈-TPA (0.36 g, yield 48.21%) was synthesized in a similar manner with MC₈ instead of MC₆Cz (scheme 1). ¹H NMR (400 MHz, Chloroform-d) δ: 8.18 (d, 1H), 7.58 (d, J = 7.7 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.31 – 7.26 (m, 6H), 7.25 – 7.18 (m, 10H), 7.15 – 7.07 (m, 12H), 7.06 – 6.99 (m, 5H), 4.23 (t, J = 6.5 Hz, 2H), 2.07 – 1.95 (m, 2H), 1.69 – 1.57 (m, 2H), 1.50 – 1.24 (m, 8H), 0.90 (t, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.51, 153.76, 151.60, 147.73, 147.67, 147.26, 147.03, 146.09, 141.43, 138.93, 138.29, 135.55, 135.47, 129.31, 128.43, 128.29, 127.95, 127.77, 126.63, 126.10, 124.42, 124.39, 124.12, 124.00, 123.87, 123.81, 123.00, 122.91, 116.78, 108.81, 68.22, 65.92, 31.90, 29.77, 29.55, 29.48, 29.34, 26.36, 22.77, 14.23, 1.11.

9-(4-(7-(4-(9H-carbazol-9-yl)phenyl)-4-(octyloxy)-9,9-diphenyl-9H-fluoren-2-yl)phenyl)-9H-carbazole (MC₈-9-NPC). MC₈-9-NPC (0.40 g, yield 54.1%) was synthesized in a similar manner with MC₈ instead of MC₆Cz, and with b instead of a (scheme 1). ¹H NMR (400 MHz, Chloroform-d) δ: 8.32 (dd, J = 7.7, 0.8 Hz, 1H), 8.20 – 8.12 (m, 4H), 7.85 – 7.71 (m, 6H), 7.66 – 7.58 (m, 4H), 7.51 – 7.35 (m, 13H), 7.34 – 7.27 (m, 10H), 7.21 (d, J = 1.3 Hz, 1H), 4.33 (t, J = 6.5 Hz, 2H), 2.13 – 2.03 (m, 2H), 1.75 – 1.63 (m, 2H), 1.54 – 1.30 (m, 8H), 0.94 (t, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.79, 154.14, 151.94, 145.87, 141.28, 140.87, 140.60, 140.47, 138.92, 138.81, 136.94, 136.71, 128.70, 128.51, 128.45, 128.42, 127.41, 127.29, 126.85, 126.73, 126.01, 124.51, 124.33, 123.46, 120.37, 120.05, 120.00, 117.25, 109.89, 109.33, 68.40, 66.09, 31.92, 29.77, 29.56, 29.50, 29.37, 26.39, 22.78, 14.23, 1.10.

2-(4-(octyloxy)-9,9-diphenyl-7-(9-phenyl-9H-carbazol-2-yl)-9H-fluoren-2-yl)-9-phenyl-9H-carbazole (MC₈-2-NPC). MC₈-2-NPC (0.37 g, yield 50.2%) was synthesized in a similar manner with MC₈ instead of MC₆Cz, and with c instead of a (scheme 1). ¹H NMR (400 MHz, Chloroform-

d) δ : 8.20 (d, $J = 8.0$ Hz, 1H), 8.17 – 8.12 (m, 4H), 7.68 – 7.55 (m, 11H), 7.53 – 7.45 (m, 5H), 7.43 – 7.38 (m, 4H), 7.32 – 7.27 (m, 7H), 7.24 – 7.18 (m, 6H), 7.09 (d, $J = 1.3$ Hz, 1H), 4.22 (t, $J = 6.3$ Hz, 2H), 2.04 – 1.92 (m, 2H), 1.69 – 1.57 (m, 2H), 1.49 – 1.23 (m, 8H), 0.89 (t, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.60, 153.70, 151.52, 146.20, 143.02, 141.53, 141.47, 141.37, 140.46, 140.05, 139.85, 138.58, 137.69, 129.97, 129.54, 128.47, 128.35, 127.56, 127.26, 127.19, 127.10, 126.72, 126.09, 125.99, 124.87, 124.25, 123.29, 123.25, 122.77, 122.55, 120.54, 120.44, 120.41, 120.22, 120.15, 119.98, 119.76, 117.91, 113.98, 109.91, 109.86, 108.49, 108.33, 68.33, 66.04, 31.95, 29.83, 29.58, 29.51, 29.37, 26.41, 22.82, 14.28, 1.17.

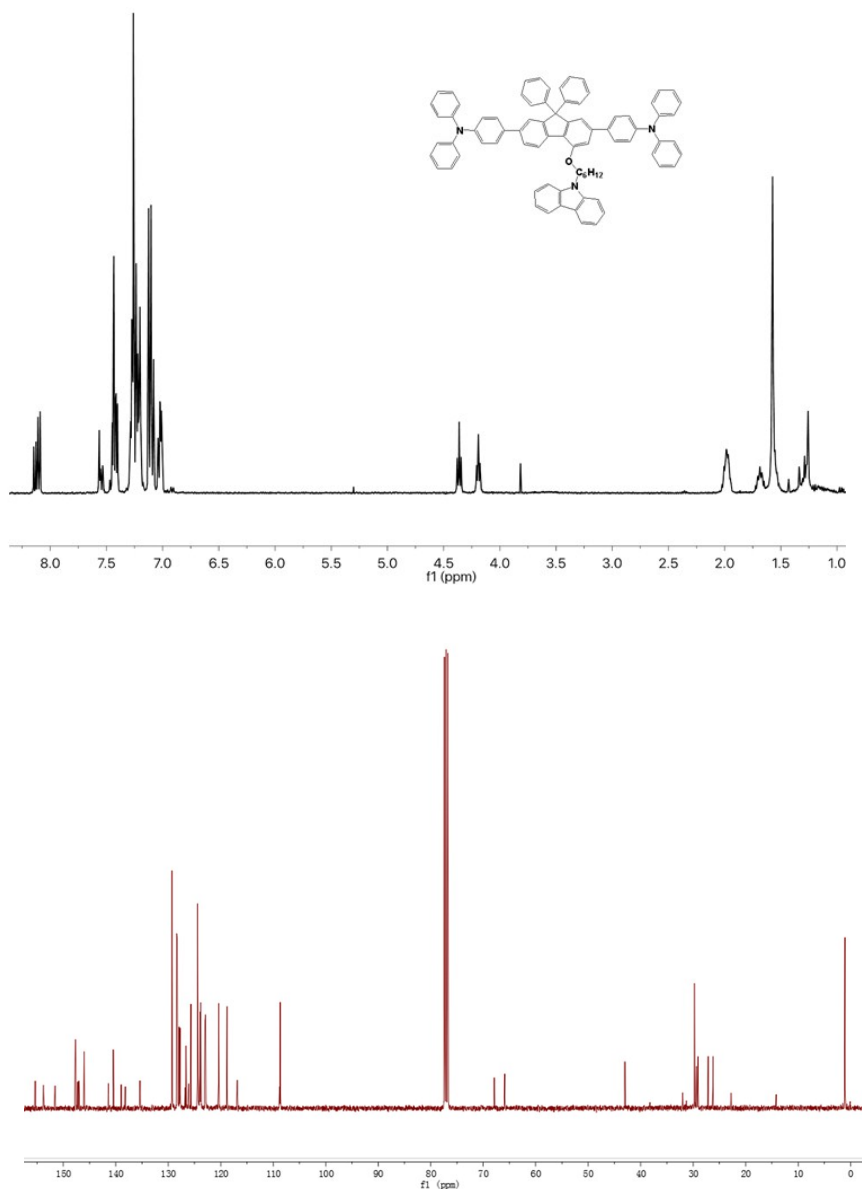


Figure S1. ^1H and ^{13}C NMR spectra of $\text{MC}_6\text{Cz-TPA}$ in CDCl_3 .

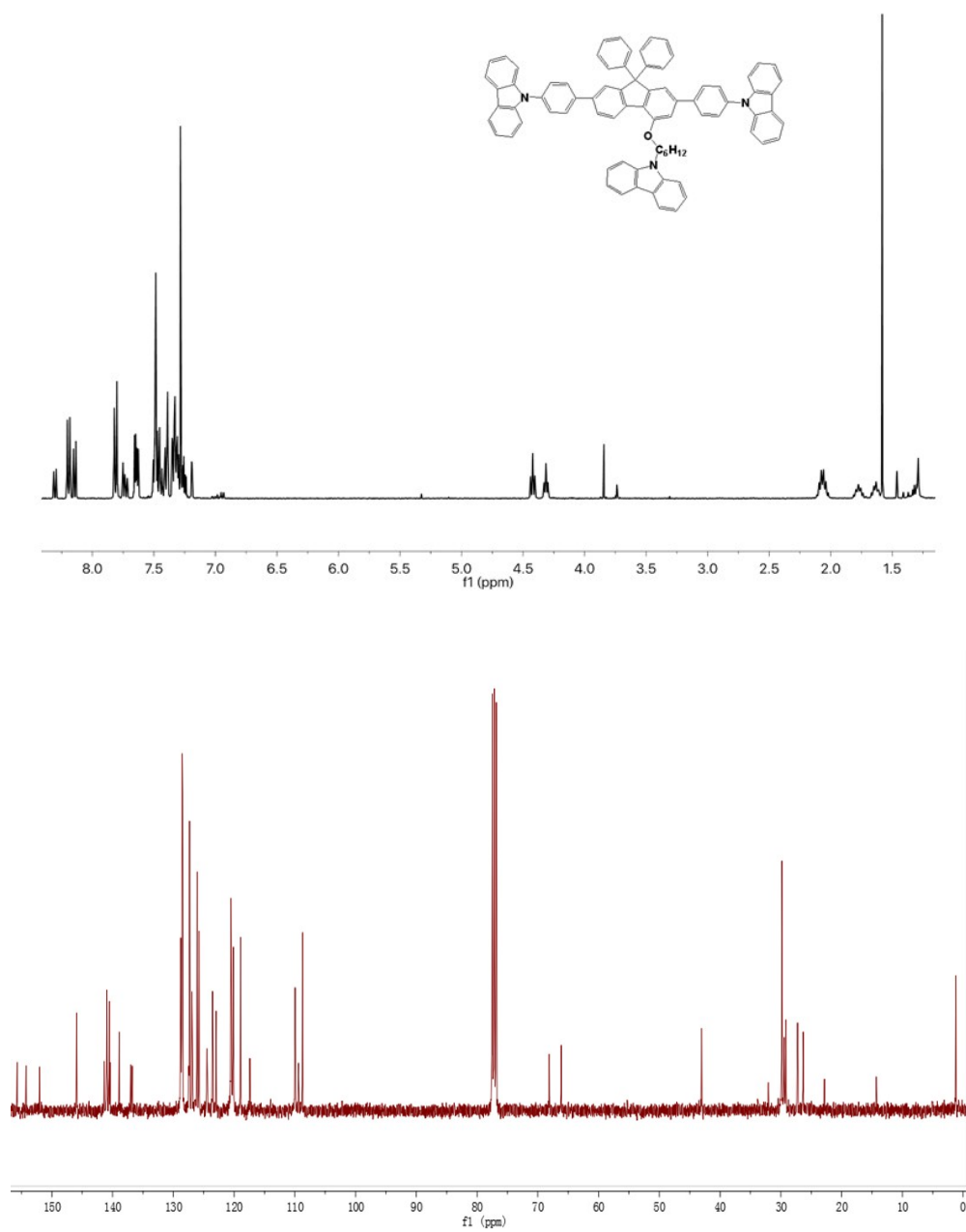


Figure S2. ¹H and ¹³C NMR spectra of MC₆Cz-9-NPC in CDCl₃.

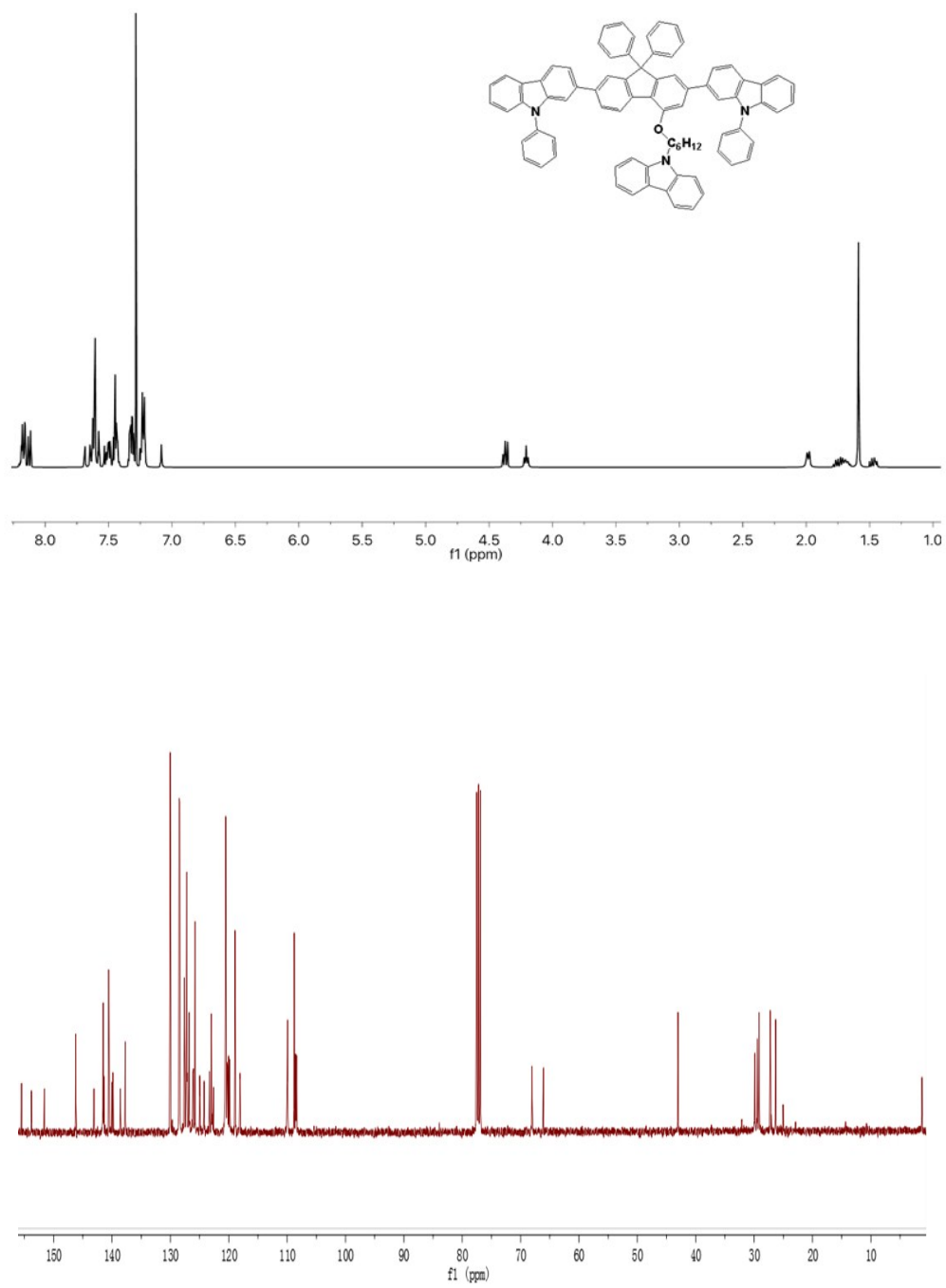


Figure S3. ¹H and ¹³C NMR spectra of MC₆Cz-2-NPC in CDCl₃.

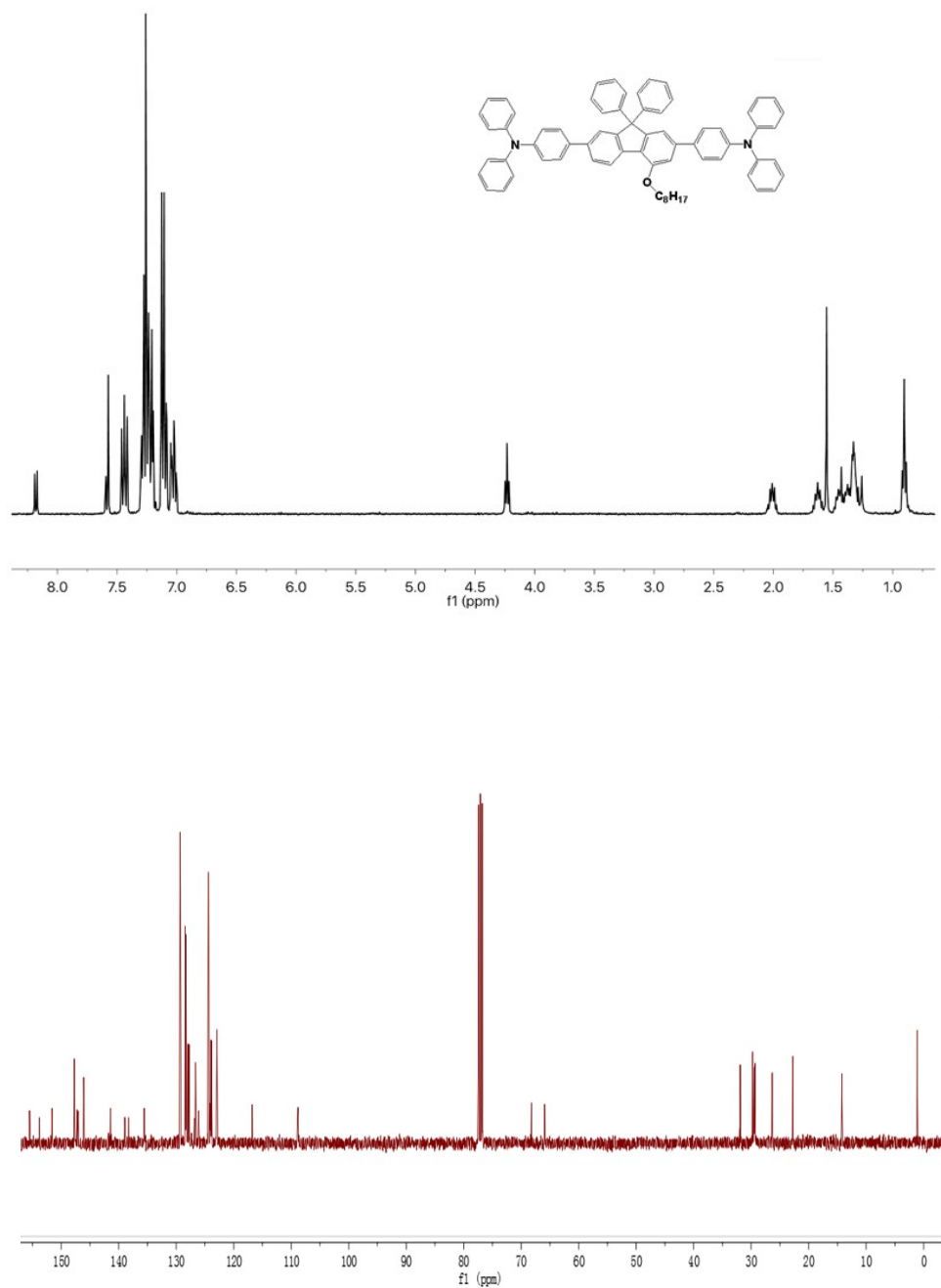


Figure S4. ¹H and ¹³C NMR spectra of MC₈-TPA in CDCl₃.

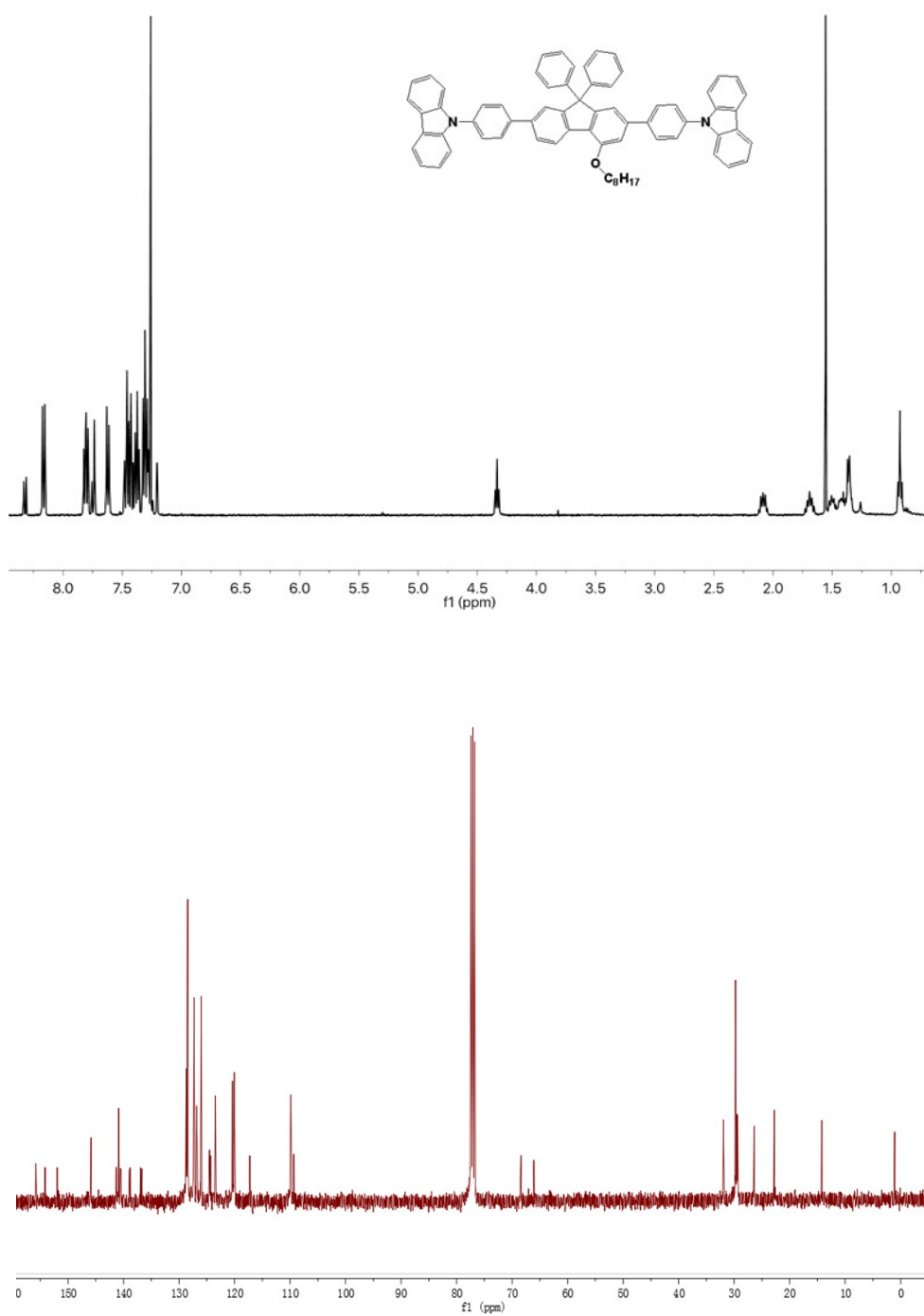


Figure S5. ¹H and ¹³C NMR spectra of MC₈-9-NPC in CDCl₃.

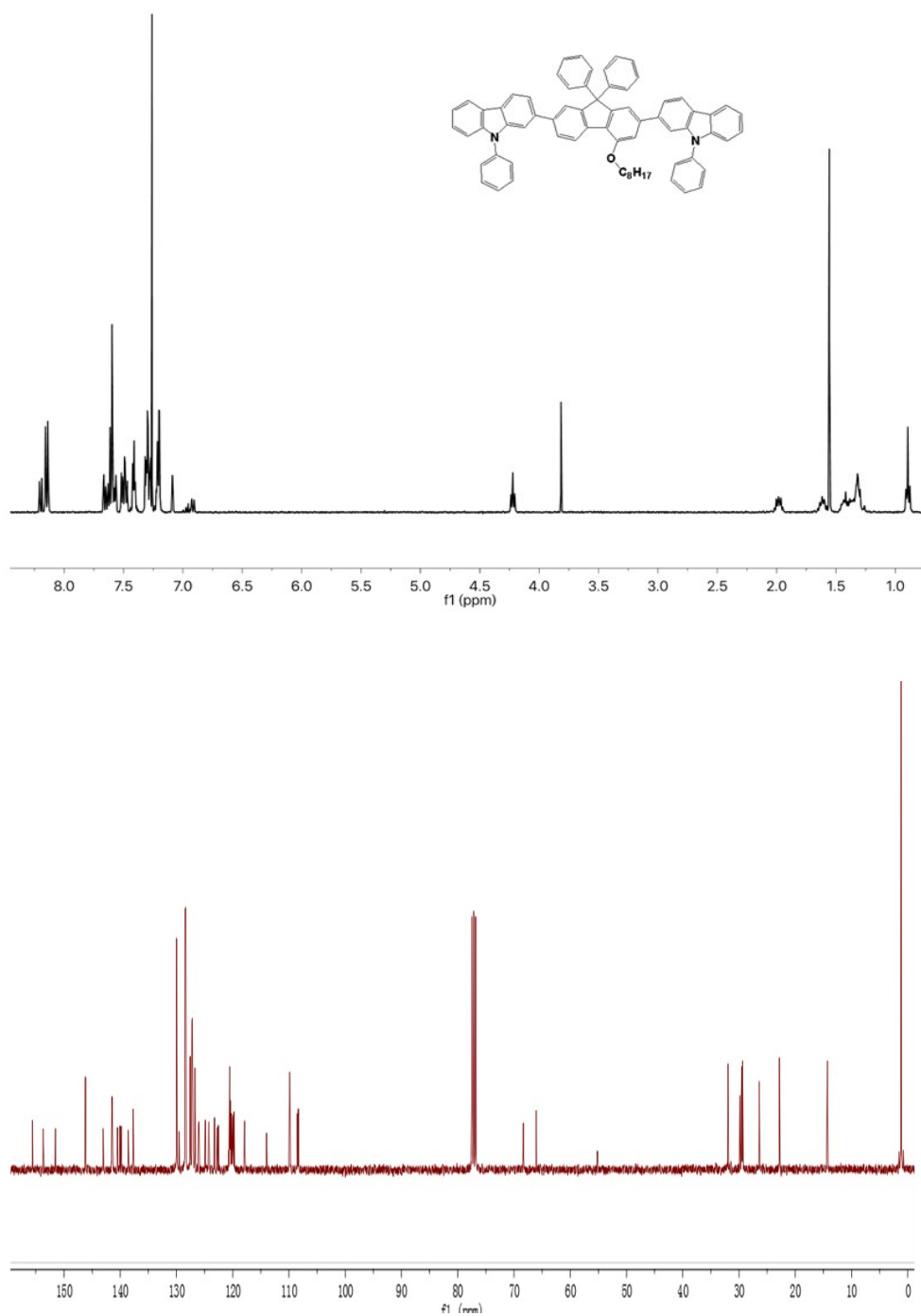


Figure S6. ¹H and ¹³C NMR spectra of MC₈-2-NPC in CDCl₃.

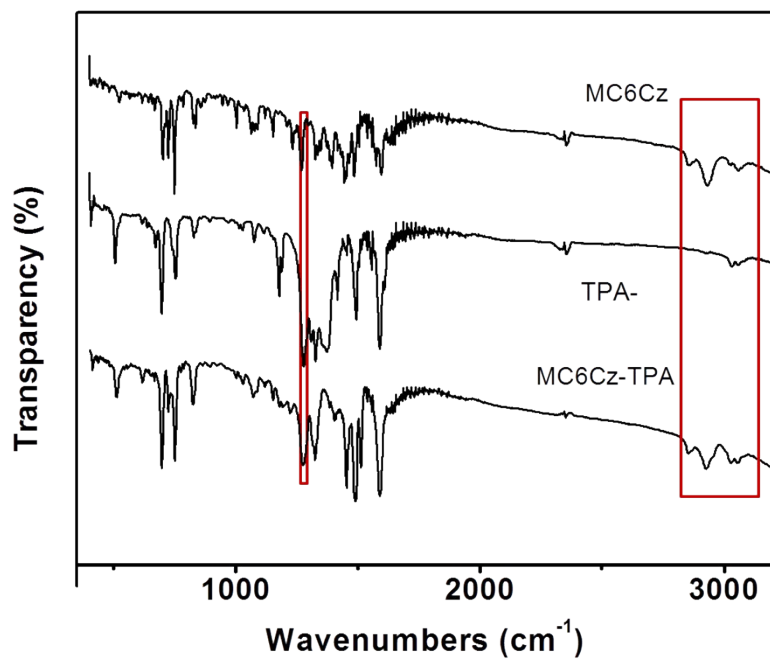


Figure S7. FTIR spectra of MC₆Cz, TPA-, MC₆Cz-TPA.

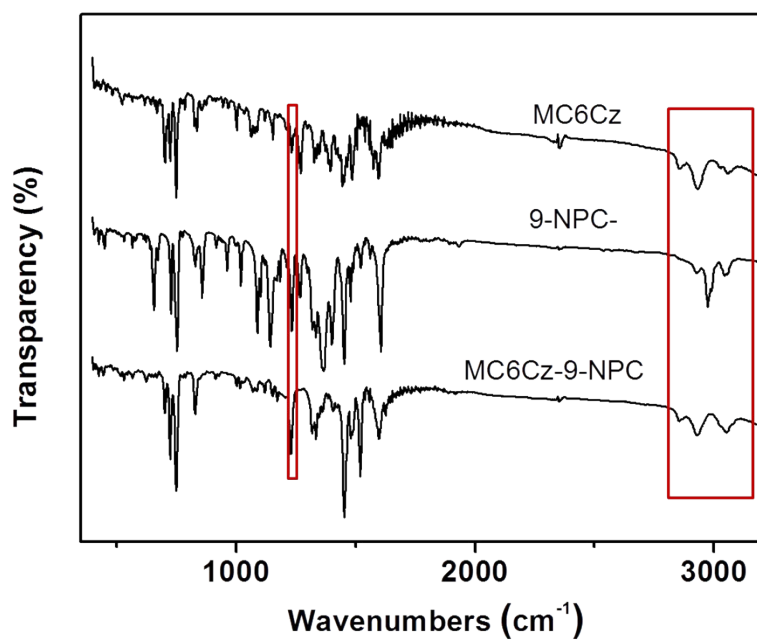


Figure S8. FTIR spectra of MC₆Cz, 9-NPC-, MC₆Cz-9-NPC.

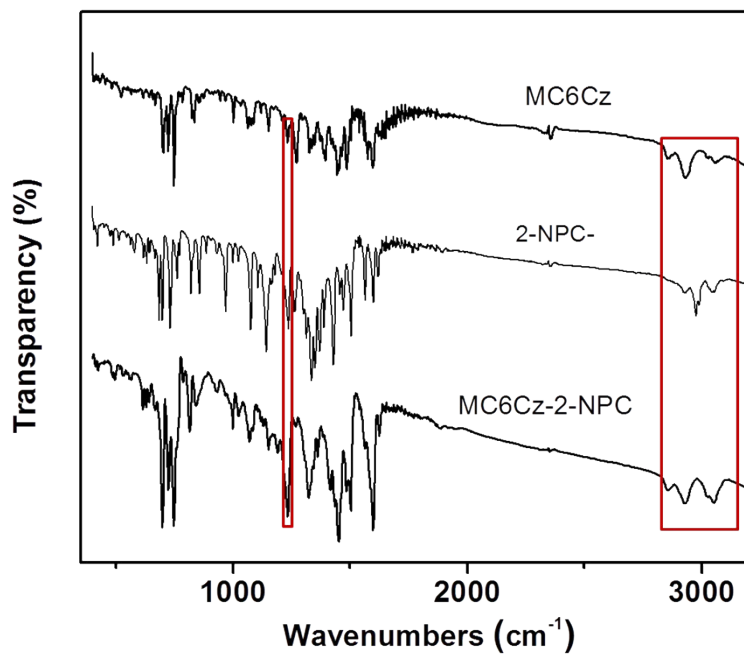


Figure S9. FTIR spectra of MC₆Cz, 2-NPC-, MC₆Cz-2-NPC.

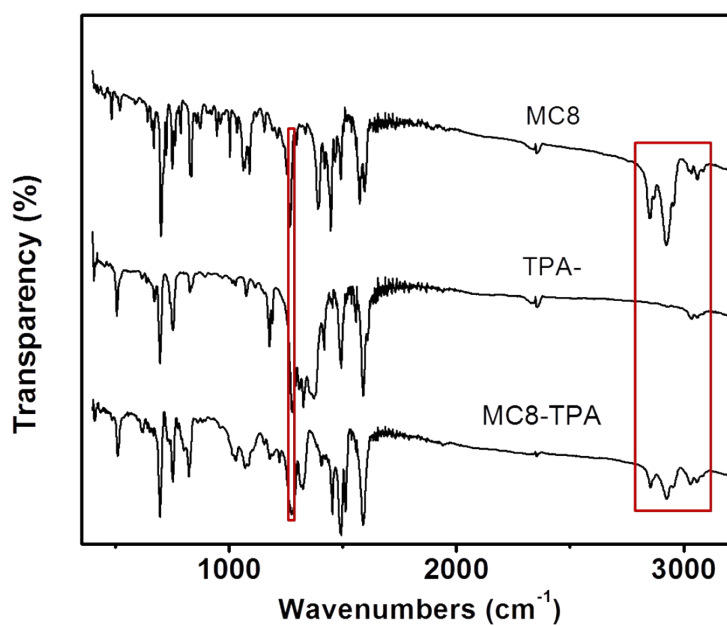


Figure S10. FTIR spectra of MC₈, TPA-, MC₈-TPA.

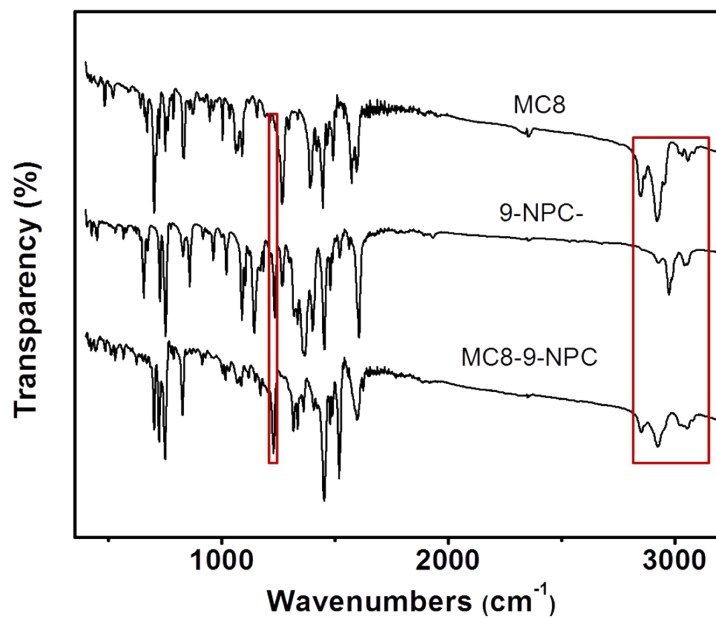


Figure S11. FTIR spectra of MC₈, 9-NPC-, MC₈-9-NPC.

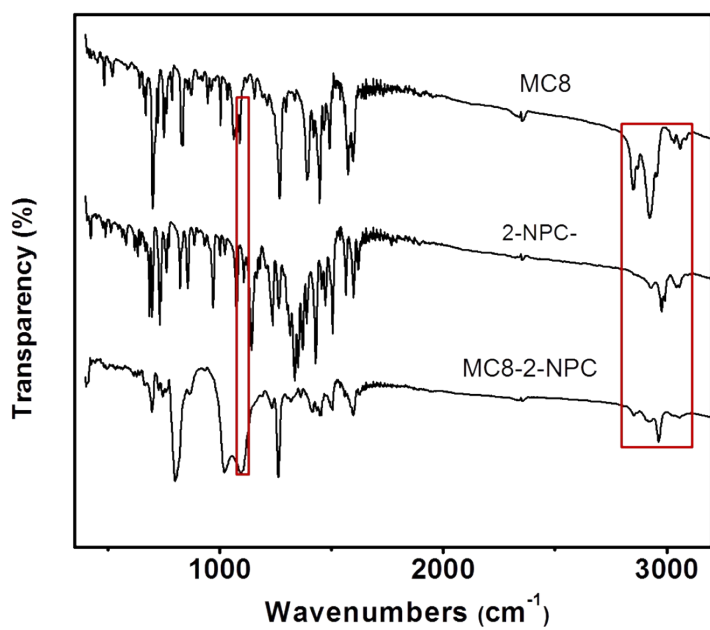


Figure S12. FTIR spectra of MC₈, 2-NPC-, MC₈-2-NPC.

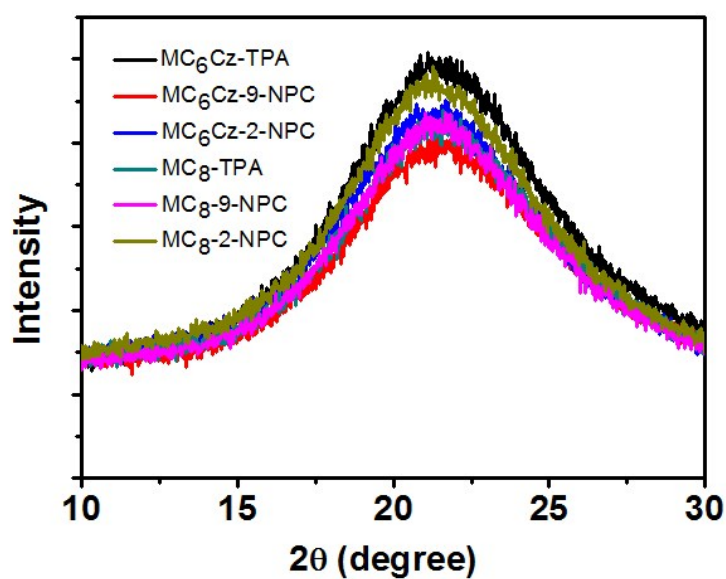


Figure S13. The XRD patterns of the 6 compounds in thin solid films spin-coated from toluene solution.

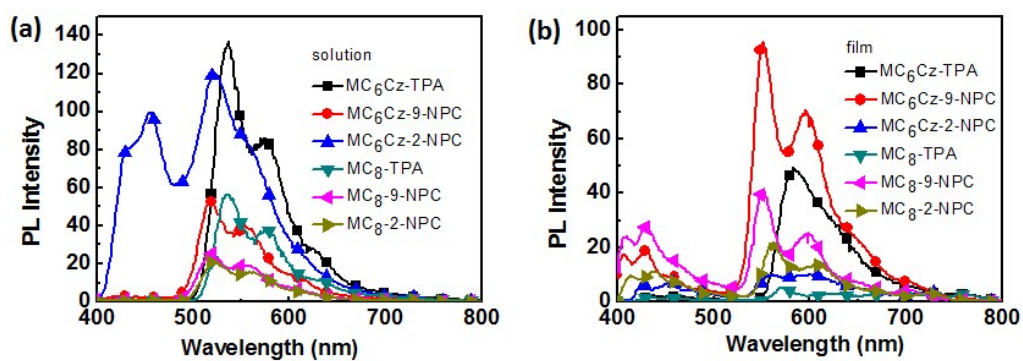


Figure S14. Phosphorescence spectroscopy of these compounds measured in toluene solutions (a) and in thin solid films spin-coated from CHCl_3 solution (b) at 77 K.

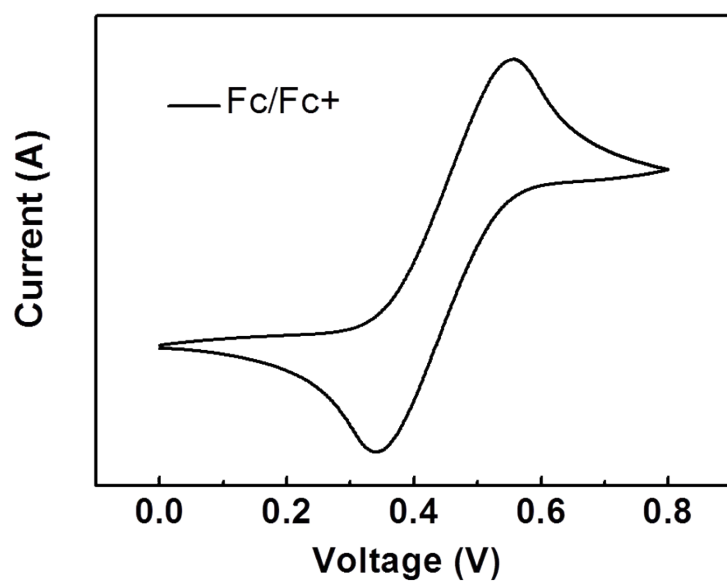


Figure S15. Cyclic voltammograms of the Fc/Fc⁺.

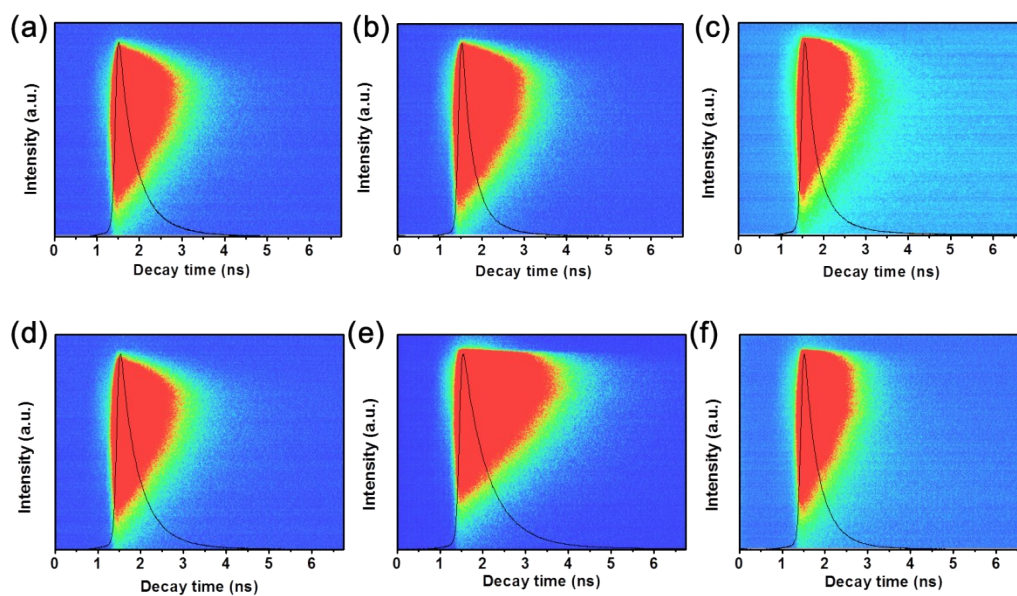


Figure S16. The time resolved PL decays curves of films.

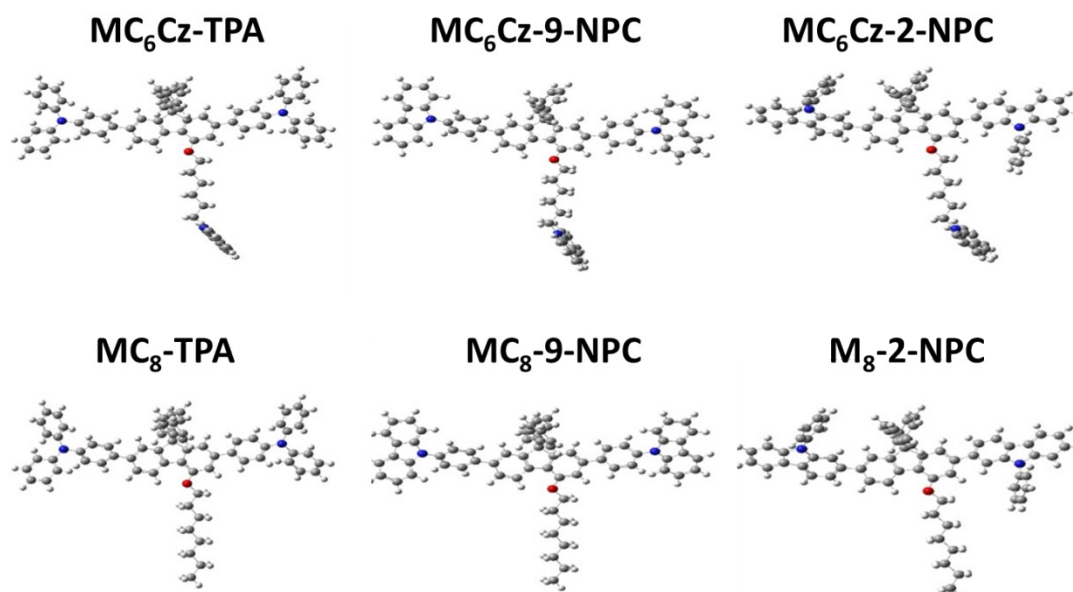


Figure S17. The optimized structures of the 6 compounds by density functional theory (DFT) calculations.

Reference

1. J.-Y. Lin, W.-S. Zhu, F. Liu, L.-H. Xie, L. Zhang, R. Xia, G.-C. Xing and W. Huang, *Macromolecules*, 2014, **47**, 1001-1007.