

Supporting Information

Solution-processed Triphenylethylene-Fluorene Fluorochromes toward Deep-blue Organic Light-emitting Diodes: Benefits of Preventing Radical Formation

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Reagents and materials

The starting material MC8 was prepared according to our previous work.¹ The catalyst tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) and thiophene-2-boronic acid pinacol ester were purchased from Alfa-Aesar and Adamas. Fluorine and methyl substituted triphenylethylene were obtained by Wittig reaction. The potassium tert-butoxide, diethyl-4-bromobenzyl phosphonate, 4,4'-dimethylbenzophenone, bis(4-fluorophenyl)-methanone and 5,5-dimethyl-1-pyrrolidone N-oxide were purchased from Alfa-Aesar and Adamas. All reagents, such as toluene and tetrahydrofuran (THF) were purified and dried according to standard procedures.

Measurements

¹H NMR and ¹³C NMR and ¹H-¹H rotating frame overhauser effect spectra were recorded on a Bruker Ultra Shield plus 400 MHz spectrometer. Mass spectra were obtained on a matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS). UV-visible absorption spectra were measured with a Shimadzu UV-1750 spectrometer at 25 °C, and steady-state photoluminescence spectra were measured using Hitachi F-4600. Photoluminescence (PL) spectra were taken with a fluorescence spectrophotometer (Shimadzu RF- 5301PC) equipped with a xenon lamp as an excitation source. The measurements were recorded in a range from 400 nm to 600 nm with excitation wavelength at 384 nm at room temperature. Thermogravimetric analysis (TGA) was acquired using a Mettler Instruments TGA. Differential scanning calorimetry (DSC) data was measured using DSC214 Polyma at a rate of 10 °C/min. 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-Bu₄NPF₆) in Dichloromethane (CH₂Cl₂) at a sweeping rate of 0.05 V/s. According to the redox onset potentials of the CV measurements, the HOMO/lowest unoccupied molecular

orbital (LUMO) energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): $\text{HOMO} = -[\text{E}_{\text{onset}} - \text{E}_{(\text{Fc}/\text{Fc}^+)} + 4.8]$ eV. The optical band-gap (E_g) estimated by absorption spectrum. The calculated LUMO by the formula of $\text{LUMO} = \text{HOMO} + E_g$. Quantum Yield (PLQY) was measured with Time-Correlated Single Photon Counting (FLS 980). All the spin-coated films of F-TrPE-MC₈, M-TrPE-MC₈, F-TrPE-MC₈_UV and M-TrPE-MC₈_UV were encapsulated by cover glasses. Transient absorption (TA) analysis of polymer films was measured with Nanosecond Transient Absorption Spectroscopy equipment (NANO-TA100). All the spin-coated films of F-TrPE-MC₈, M-TrPE-MC₈, F-TrPE-MC₈_UV and M-TrPE-MC₈_UV were encapsulated by cover glasses. The film morphologies of films were recorded with a Park System AFM by tapping mode. All the thick film was spin-coated with a speed of 1500 r/min (60 s).

EPR were measured with EMXplus EMXmicro.

Fabrication and Characterization of OLEDs:

All OLEDs devices were prepared and characterized following the process as follows. The ITO substrates were 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 before spincoating. Firstly, a 40 nm thick PEDOT:PSS was spin-coated with a speed of 3000 r/min (60 s) and then annealed at 120°C for 15 minutes. Then, the emitting layer was spin-coated from toluene solution (10 mg/mL) with a speed of 1500 r/min (60 s) and annealed at 80°C for 20 minutes in nitrogen-filled glovebox. And the thickness of F-TrPE-MC₈ and M-TrPE-MC₈ spin-coated film is estimated about 40 and 45 nm, respectively. Finally, the residue layers, such as 20 nm TPBi, 1 nm LiF, and 100 nm Al, were deposited by thermal evaporating at a pressure below 1×10^{-5} mbar. The J – L – V curves were recorded using a combination of a Keithley source meter (model 2602) and a luminance meter. The EL spectra of the devices were measured using a PR-655 spectrophotometer. All the measurements were taken in the ambient condition at room temperature.

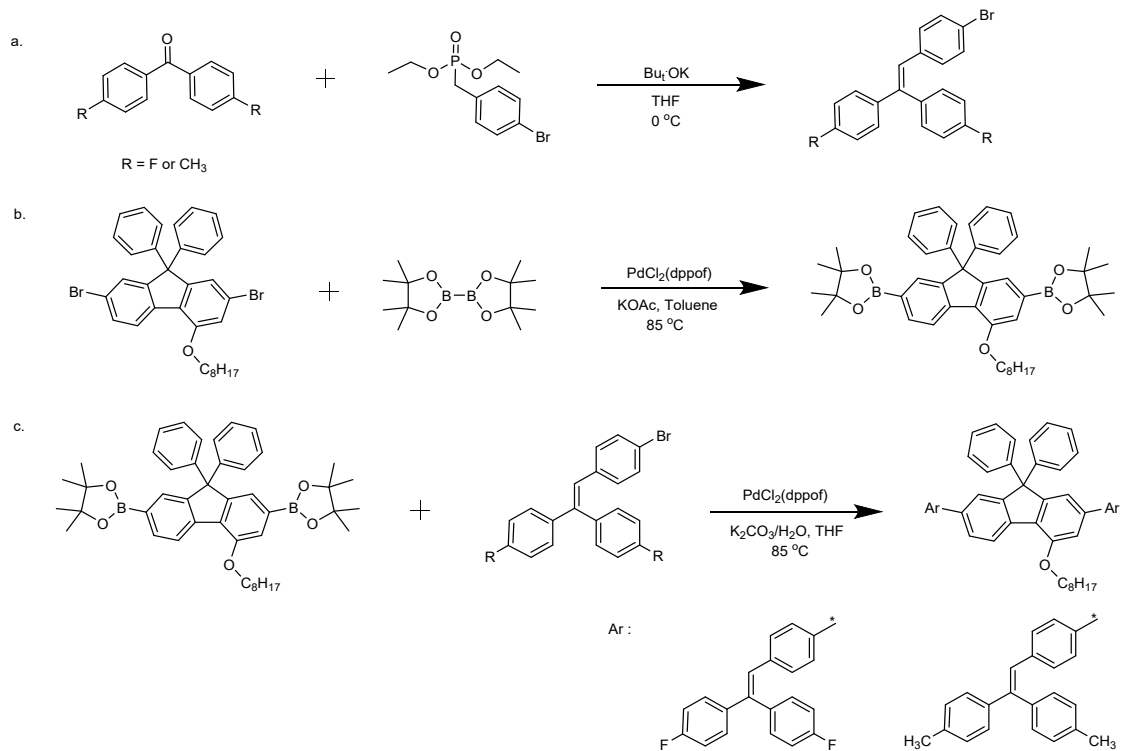
Preparation of solutions and films:

F-TrPE-MC₈ and M-TrPE-MC₈ solutions with different concentrations in Tol solvent were carried out by dissolving the conjugated molecules in the organic solvents spontaneously overnight. The preparation of solutions in EPR: F-TrPE-MC₈ and M-TrPE-MC₈ were dissolved in toluene solution and prepared to 20 mg/ml; DMPO was dissolved in toluene solution and prepared to molality of 100 mM. In use, 0.1ml of prepared DMPO was added to 0.9ml of F-TrPE-MC₈ or M-TrPE-MC₈ solution.

Fabrication films: Quartz substrates (1.5 x 1.5 x 1 mm) were first dipped in a Piranha solution (H₂SO₄/H₂O₂ ¼ 3:1) for 4 h until solutions returned to room temperature and then cleaned in ultrasonic baths by using deionized water, ethanol, isopropanol, and acetone in sequence, and finally dried with nitrogen gas. Unless there is a special explanation, the films for characterization were prepared by spin coating the toluene solutions under the speed of 1500 r/min for 60 s. The thicknesses of F-TrPE-MC₈ and M-TrPE-MC₈ toluene solution spin-coating films are 40 nm and 45 nm, respectively.

Films encapsulation: Films were encapsulated under nitrogen atmosphere using UV curable adhesive and cover glass. The films were encapsulated by a cover glass to isolate the oxygen.

Ultraviolet radiation of films: Except particularly illustration, all of the films were radiated with ultraviolet (365 nm) in approximately 1000 μW/cm².



Scheme S1. Synthesis and molecular structures of the two compounds: F-TrPE-MC₈ and M-TrPE-MC₈

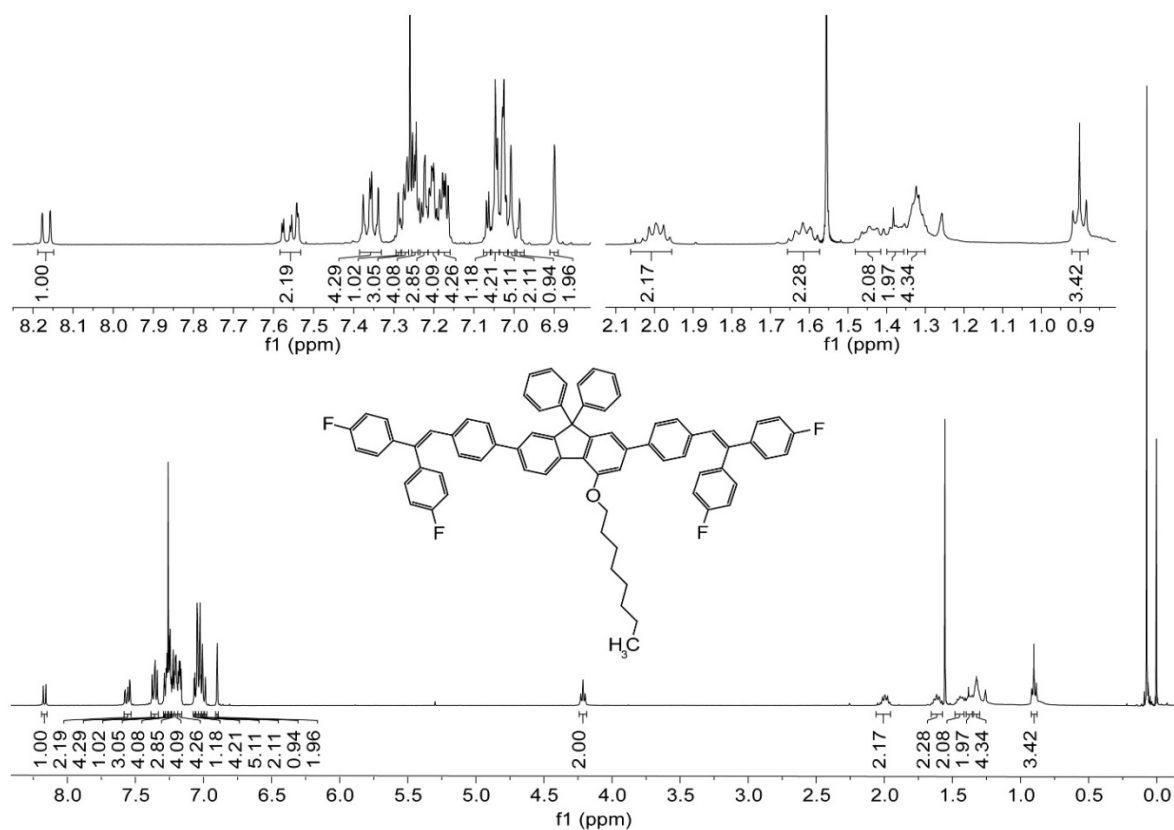


Figure S1. ¹H NMR spectra of F-TrPE-MC₈ in CDCl₃.

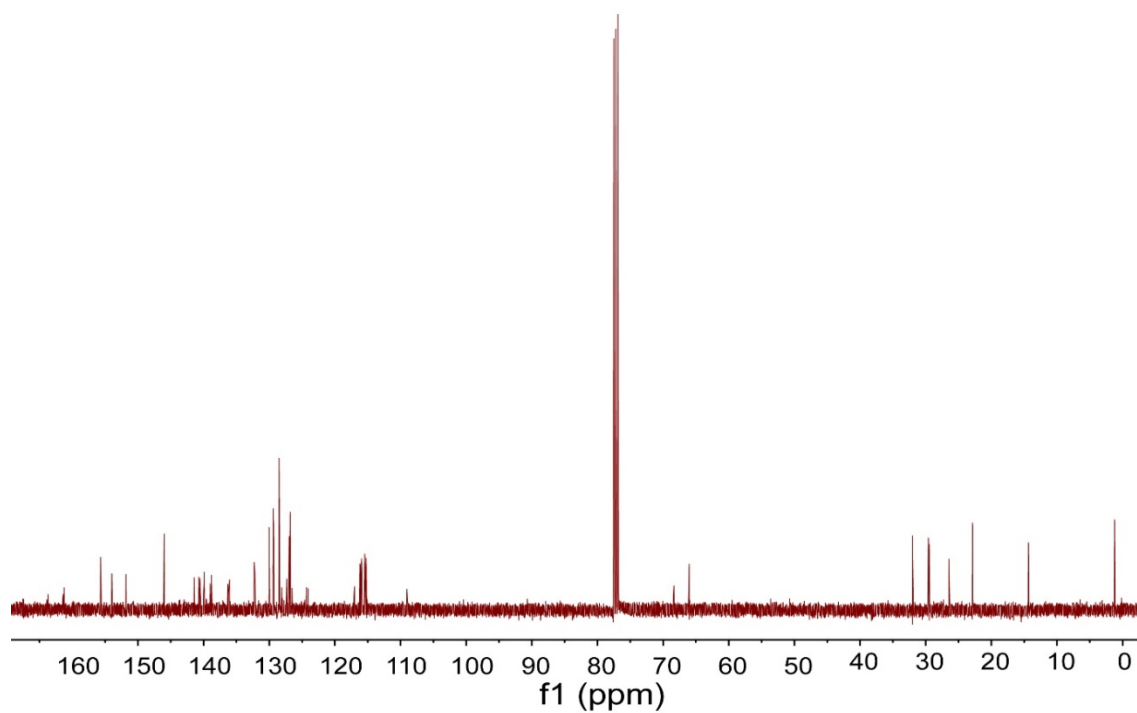


Figure S2. ^{13}C -NMR spectrum of F-TrPE- MC_8 in CDCl_3 .

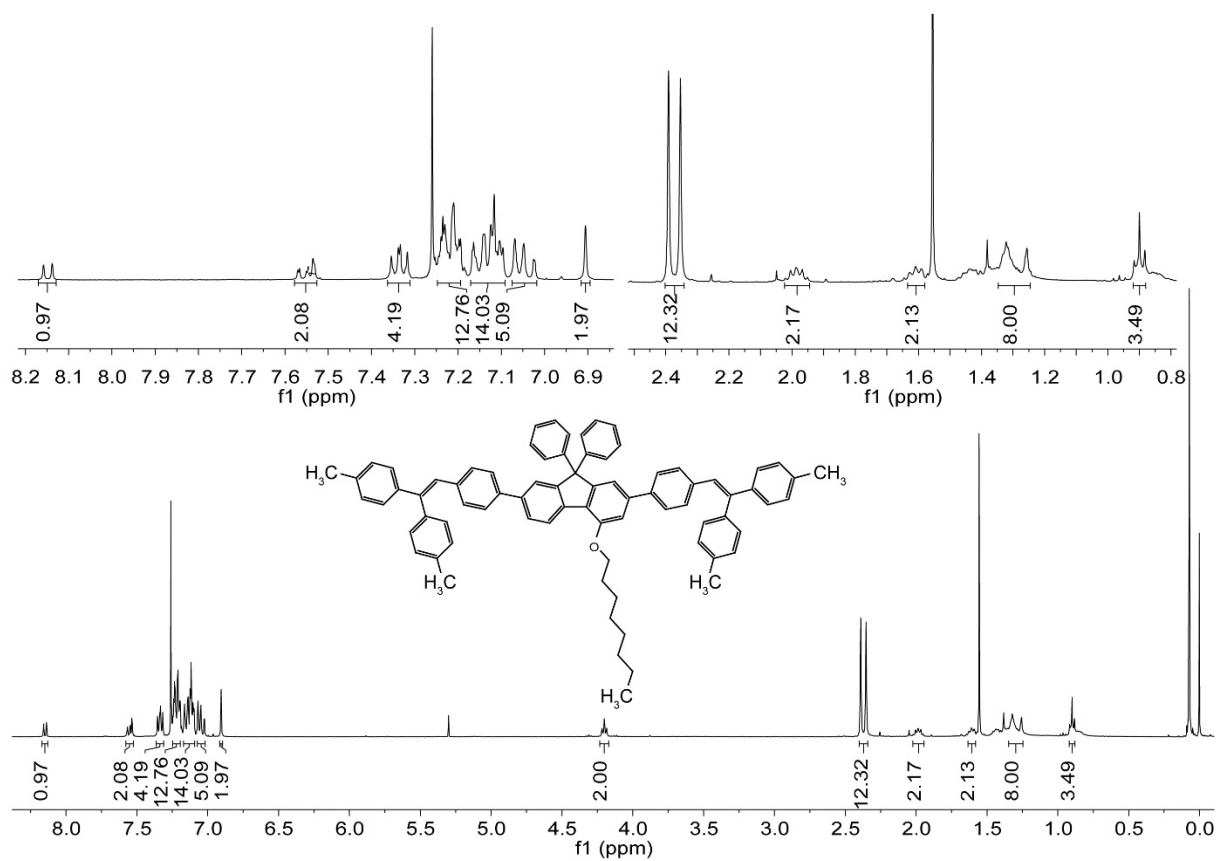


Figure S3. ^1H NMR spectra of M-TrPE- MC_8 in CDCl_3 .

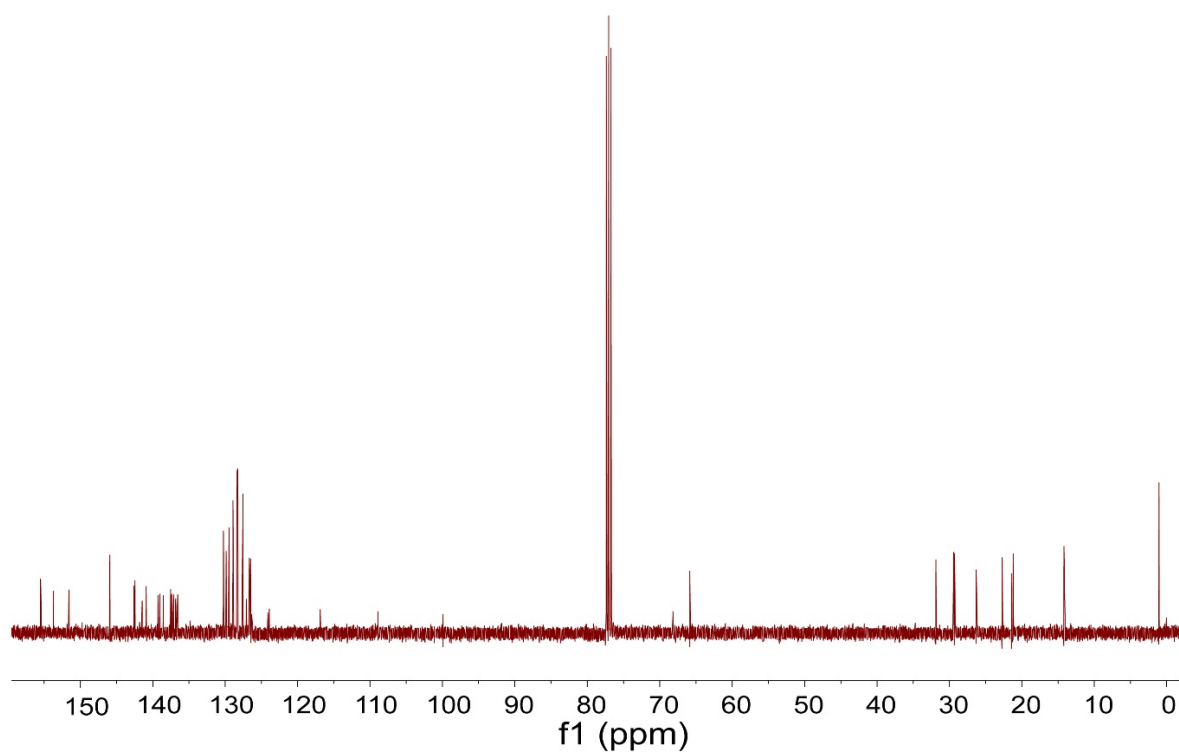


Figure S4. ^{13}C -NMR spectrum of M-TrPE-MC₈ in CDCl₃.

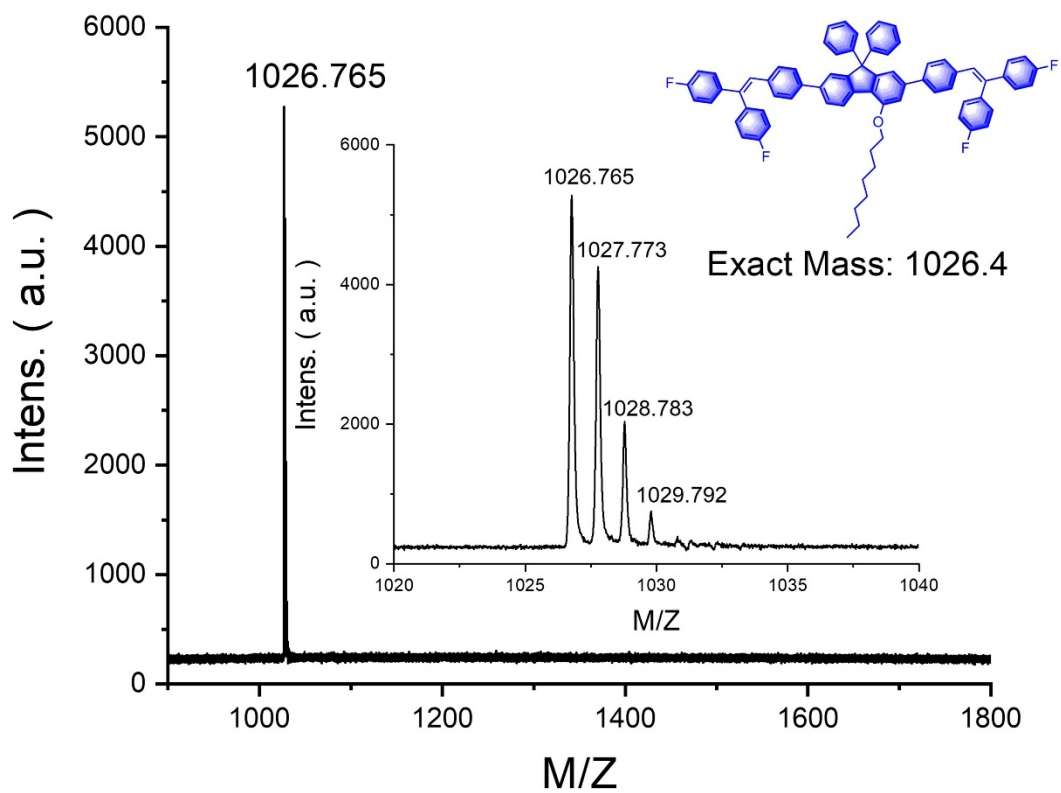


Figure S5. MALDI-TOF mass curves of F-TrPE-MC₈.

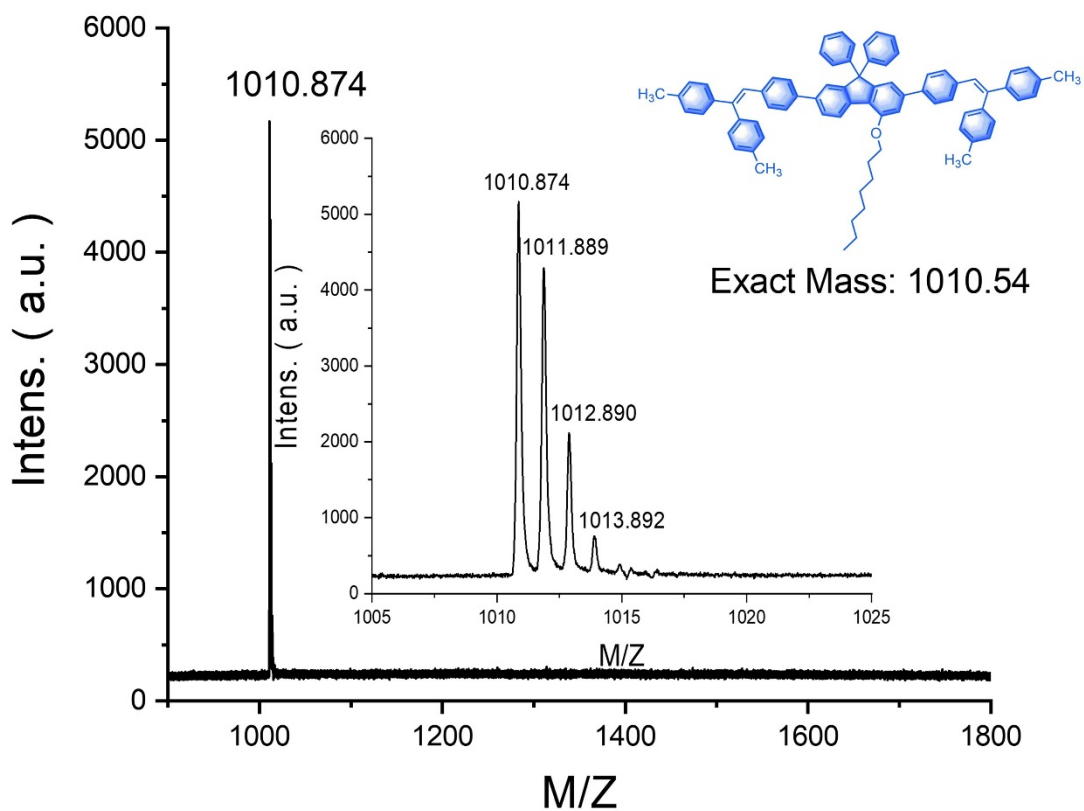


Figure S6. MALDI-TOF mass curves of M-TrPE-MC₈.

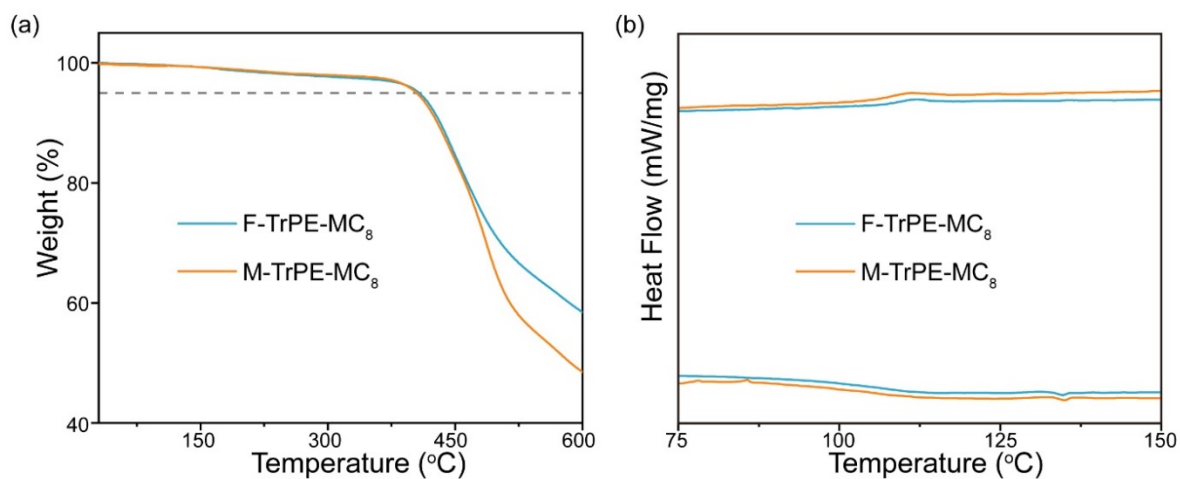


Figure S7. (a) TGA curves of the two compounds. (b) DSC curves of the two compounds measured at a heating rate of 10 °C min⁻¹ under N₂.

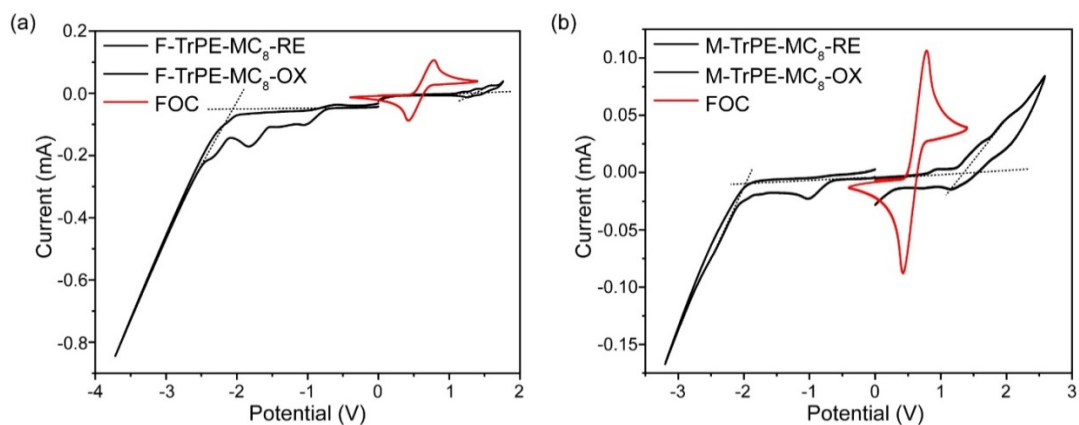


Figure S8. Cyclic voltammograms curves of F-TrPE-MC₈ (a) and M-TrPE-MC₈ (b)

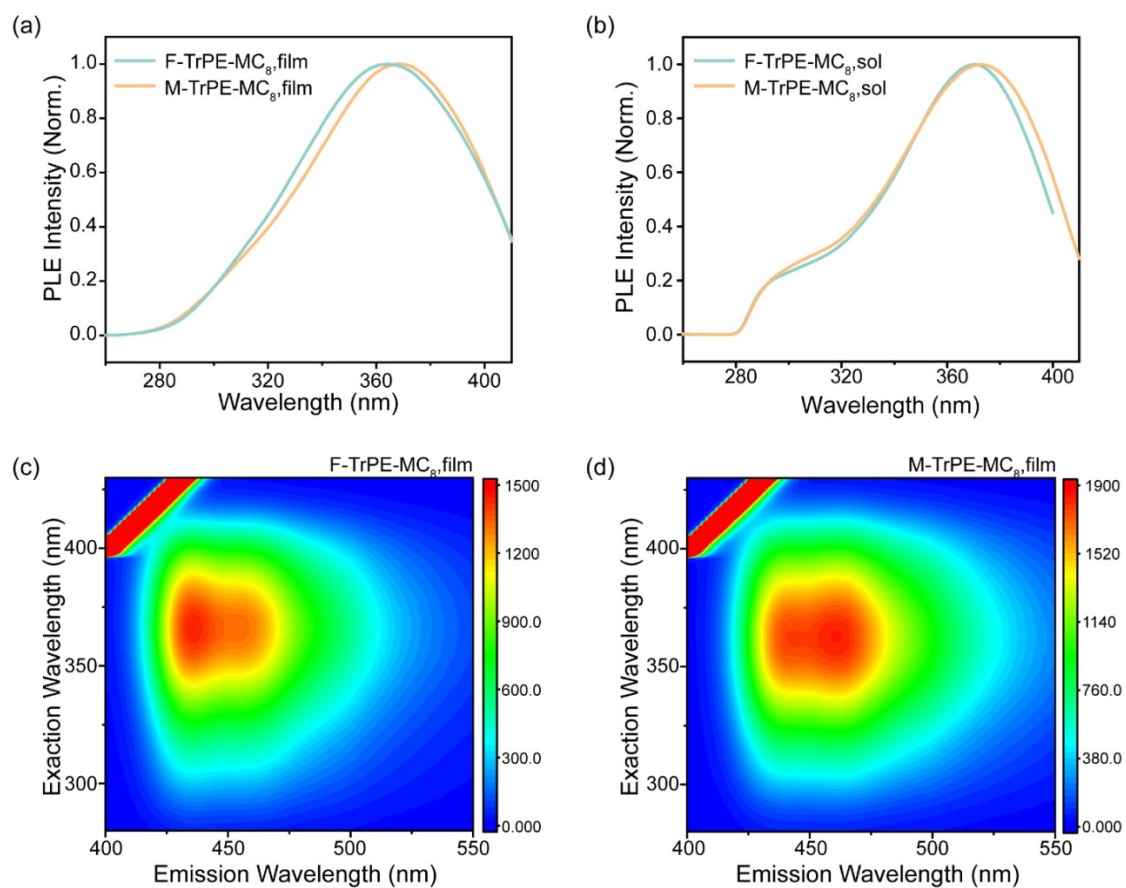


Figure S9. Excitation spectra of the tow compounds for spin-coating film (a) and diluted solution (b). PL-Mapping spectra of F-TrPE-MC₈ (c) and M-TrPE-MC₈ (d) for spin-coating films.

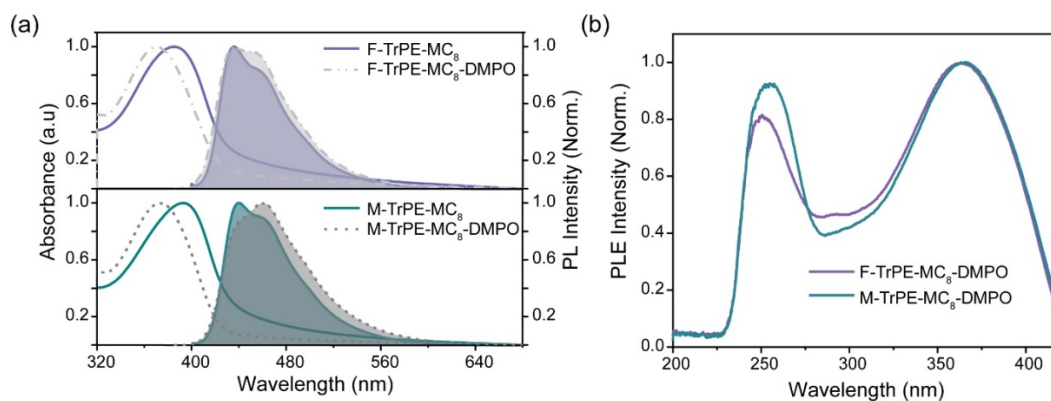


Figure S10. Absorbance and PL spectra of F-TrPE-MC₈-DMPO and M-TrPE-MC₈-DMPO films spin-coating from toluene solution (a). Exaction spectra F-TrPE-MC₈-DMPO and M-TrPE-MC₈-DMPO for spin-coating film (b).

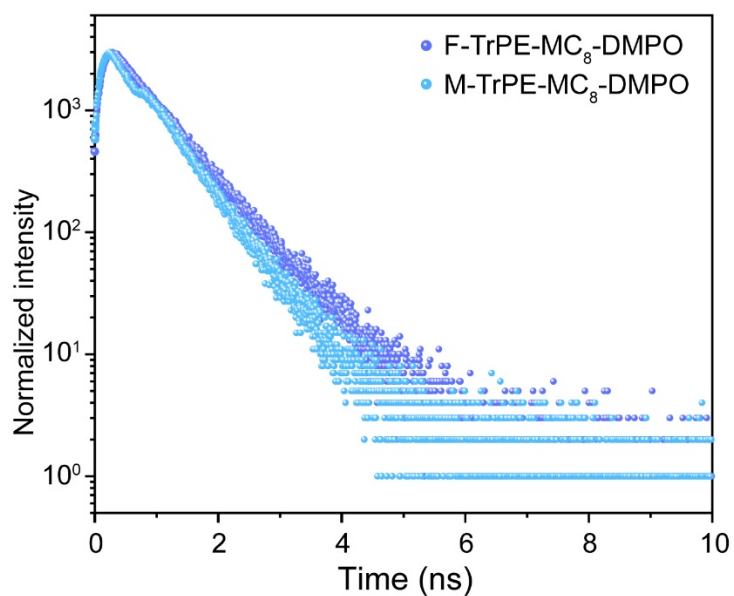


Figure S11. TCSPC measurement for solution of F-TrPE-MC₈-DMPO and M-TrPE-MC₈-DMPO for spin-coating film, collected at the peak wavelength.

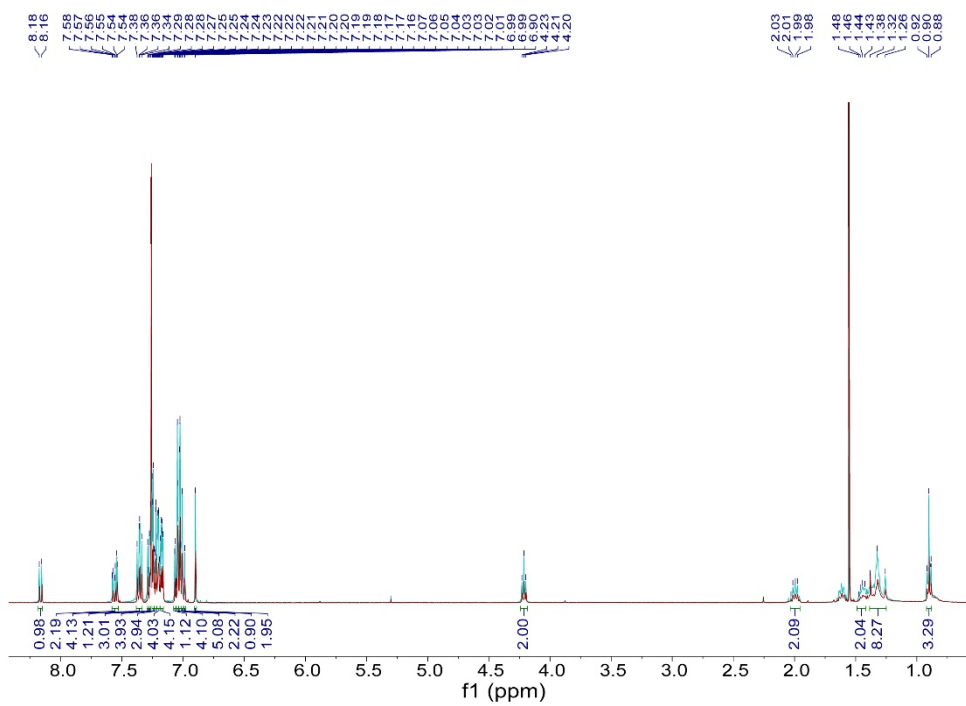


Figure S12. ^1H NMR spectra of F-TrPE-MC₈ with (blue line) and without (brown line) ultraviolet irradiation in CDCl₃.

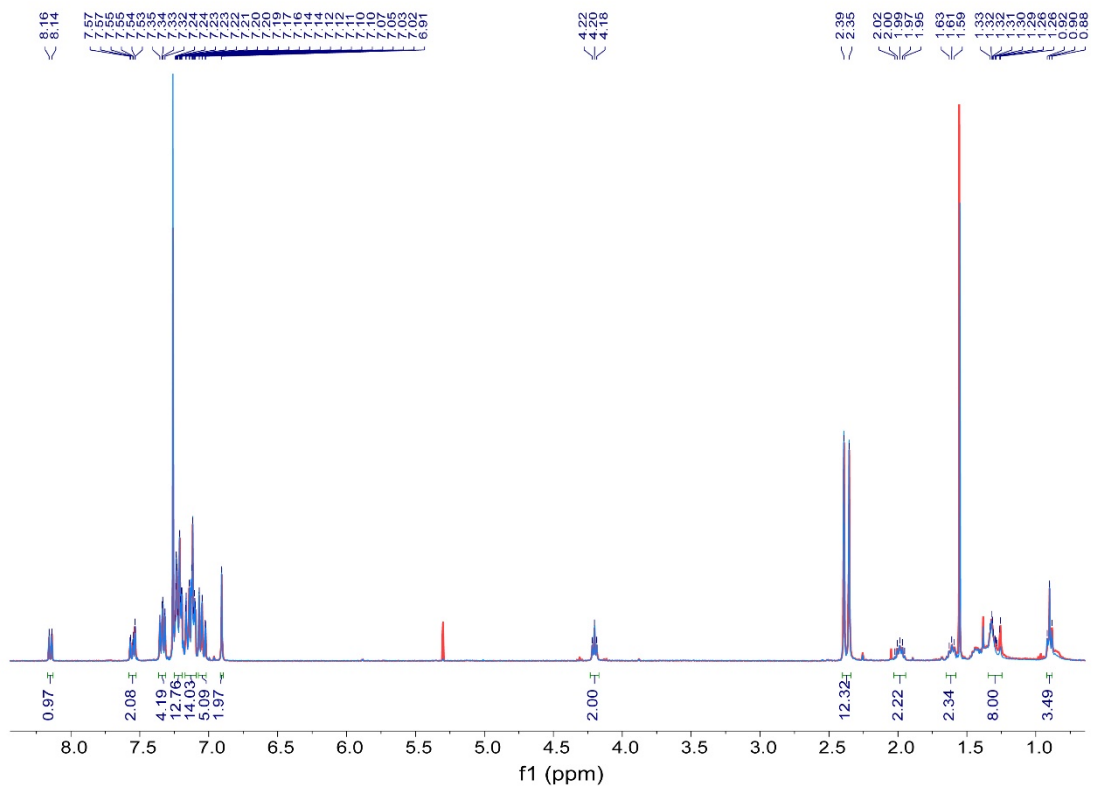


Figure S13. ^1H NMR spectra of M-TrPE- MC_8 with (pink line) and without (blue line) ultraviolet irradiation in CDCl_3 .

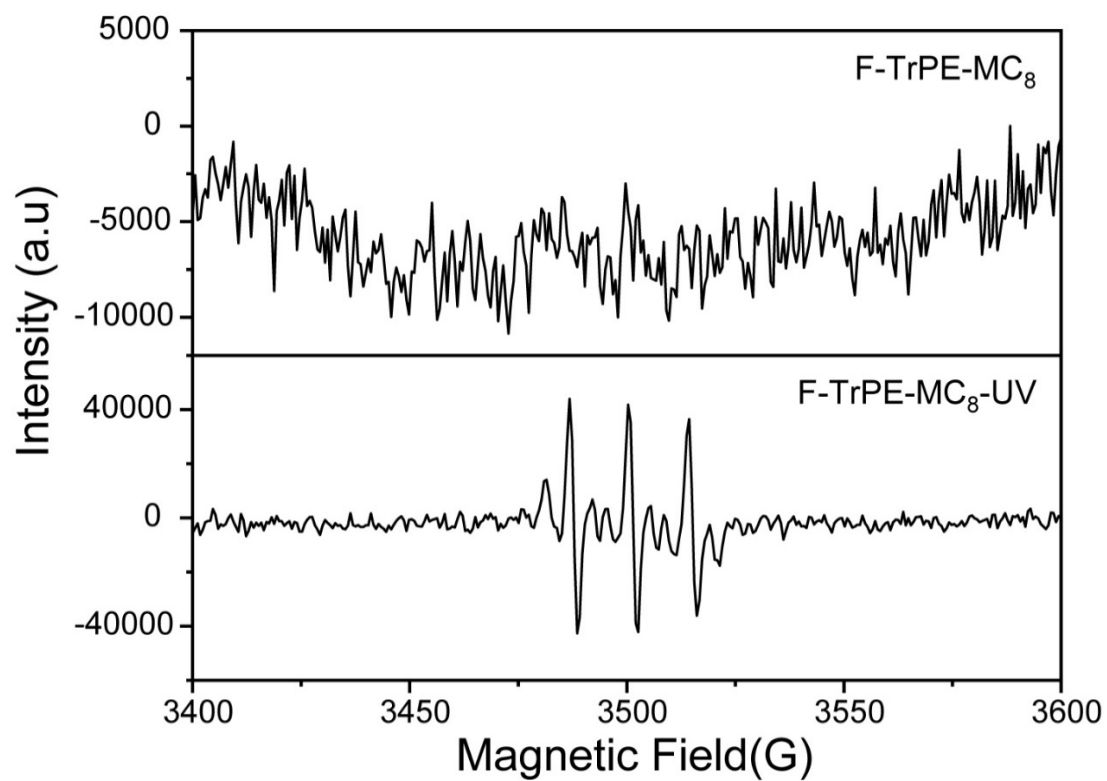


Figure S14. EPR spectra for F-TrPE-MC₈-DMPO with ultraviolet or not.

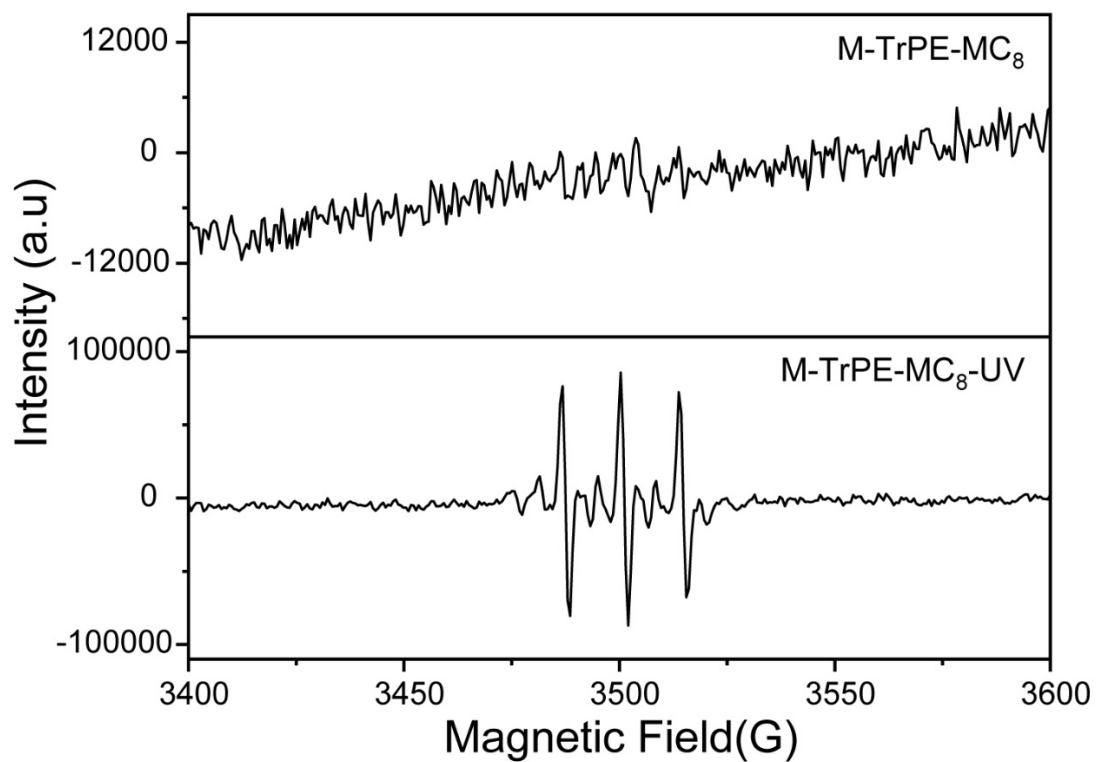


Figure S15. EPR spectra for M-TrPE-MC₈-DMPO with ultraviolet or not.

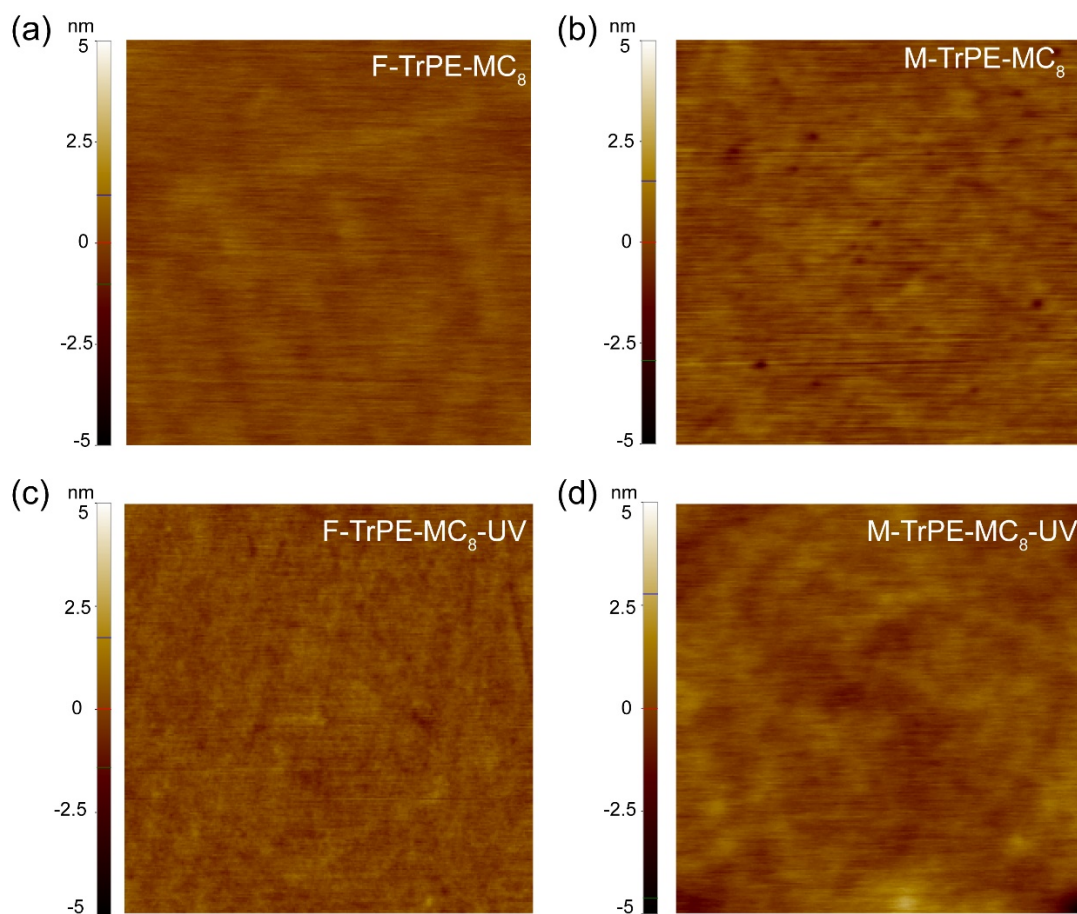


Figure S16. AFM topography of the tow compounds in different conditions spin-coated films: F-TrPE-MC₈ (a), M-TrPE-MC₈ (d), F-TrPE-MC₈_UV (c) and M-TrPE-MC₈_UV (d). The scale bar is about $5 \times 5 \mu\text{m}$.

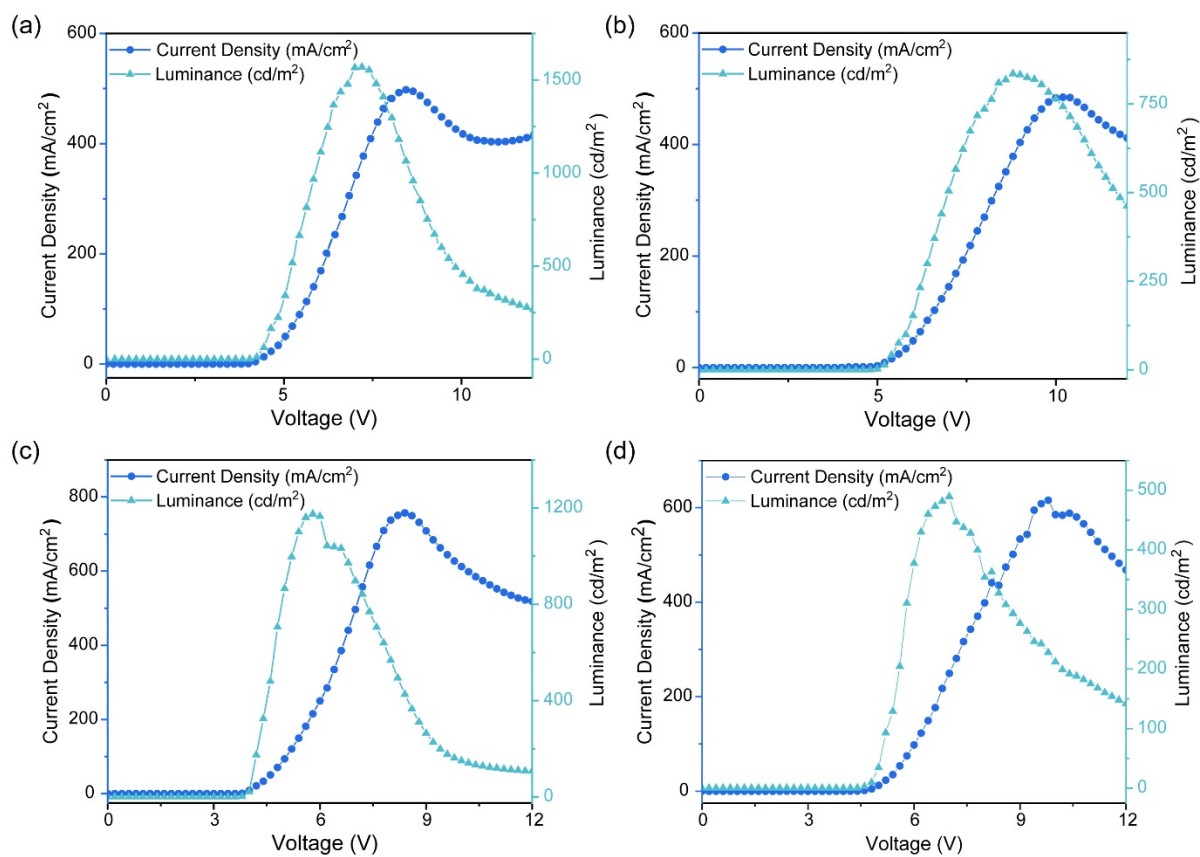


Figure S17. Current density-Voltage-Luminance characteristics of conventional OLEDs based on F-TrPE-MC₈ (a), M-TrPE-MC₈ (b), F-TrPE-MC₈_UV (c) and M-TrPE-MC₈_UV (d) films.

Table S1. The fundamental optical properties of F-TrPE-MC8-DMPO and M-TrPE-MC8-DMPO for spin-coating film.

	λ_{ab} (nm)	λ_{em} (nm)	λ_{ex} (nm)	Φ_F (%)	τ_{FL} (ns)	K_r (s ⁻¹)	K_{nr} (s ⁻¹)
F-TrPE-MC ₈ -DMPO	386	435/454	255/363	38.8	0.71	5.43×10 ⁸	8.56×10 ⁸
M-TrPE-MC ₈ -DMPO	393	441/460	250/365	35.6	0.65	5.45×10 ⁸	9.88×10 ⁸

1. J.Y Lin, W.S. Zhu, F. Liu, et al. *Macromolecules*, 47 (2014), 1001-1007.