Supporting Information

A Radical Polymer with Efficient Deep-Red Luminescence in Condensed State

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1. Materials and Methods.

1.1 General.

General: All reagents and solvents were purchased from commercial sources and used as received unless otherwise stated. Chromatographic separations were carried out using silica gel (200-300 mesh). The ^{1}H nuclear magnetic resonance (NMR) spectra were obtained in deuterated methylene chloride (CH_2Cl_2) or chloroform ($CHCl_3$) with a Bruker Avance-III 500 NMR spectrometer at ambient temperature. Fourier transform infrared spectroscopy (FTIR) spectra of radicals were recorded with Brucker VERTEX 80V. MALDI-TOF mass spectra were recorded on a Brucker Autoflex speed TOF/TOF mass spectrometer with DCTB as a matrix. EPR spectra were recorded on a Bruker ELEXSYS-II E500 CW-EPR spectrometer at ambient temperature. Thermal gravimetric analysis (TGA) was carried out on the Pyris1 TGA thermal analysis system at a heating rate of 20°C min^{-1} in a nitrogen atmosphere and air. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC204 instrument at a heating rate of 10℃ min^{-1} from 20 to 300℃ inanitrogen atmosphere. Elemental analysis was conducted on an Elementar (Variomicro cube) instrument. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a shimadzu UV-2550 spectrophotometer. Fluorescence spectra were performed using a RF-5301 PC spectrophotometer. The CV measurements were performed using an electrochemical analyzer (CHI660C, CH Instruments, USA). A glass carbon disk was used as the working electrode. A platinum wire acted as the counter electrode and Ag/Ag+ acted as the reference electrode together with the redox couple ferrocenium/ferrocene as the internal standard at the rate of 50 or

100 mV·s^{-1}. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in anhydrous dichloromethane (0.1 M) were used as the supporting electrolyte for negative and positive scan respectively. An Edinburgh fluorescence spectrometer (FLS980) was used for the fluorescence decay and absolute fluorescence measurements. The lifetime of the excited states was measured by the time-correlated single photon counting method (detected at the peak of the PL) under the excitation of a laser (375 nm) with a pulse width of 50 ps. The number- and weight-average molecular weights of the polymers were determined by GPC using a Waters 410 instrument with polystyrene as standard and THF as eluent.

Magnetic measurements were performed on a Quantum Design 6.5 Tesla SQUID-VSM system with a temperature range of 2-300 K and an applied field of 1000 Oe. As can be seen from the original data (Fig. S1a), there is a contribution of diamagnetism in the magnetic data. Hence, the fitting result did not obey Curie-Weiss law (Fig. S1b). At first, in order to eliminate the contribution of diamagnetism, the original data is fitted by the equation (Fig. S1c):

$$\chi_m = C/\ (T-\theta) + C_0 \qquad (1)$$

The diamagnetic constant C_0 = -0.123 was obtained. Then, after subtracting the diamagnetic constant from the original data, the Curie constant (*C)* and Weiss temperature (*θ)* were gotten by fitting with the Curie-Weiss law (Fig. S1d):

$$\chi_m = C/(T-\theta) \qquad (2)$$

Where, C = 1.408 emu K mol-1 and θ = -0.908 K.

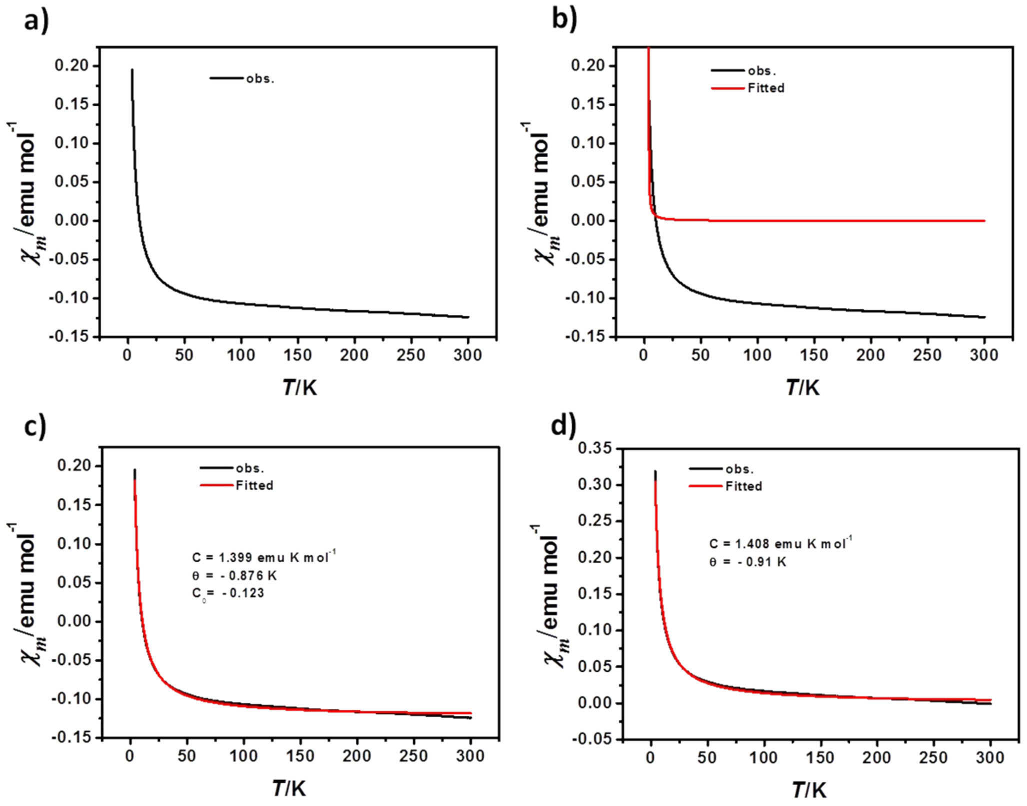
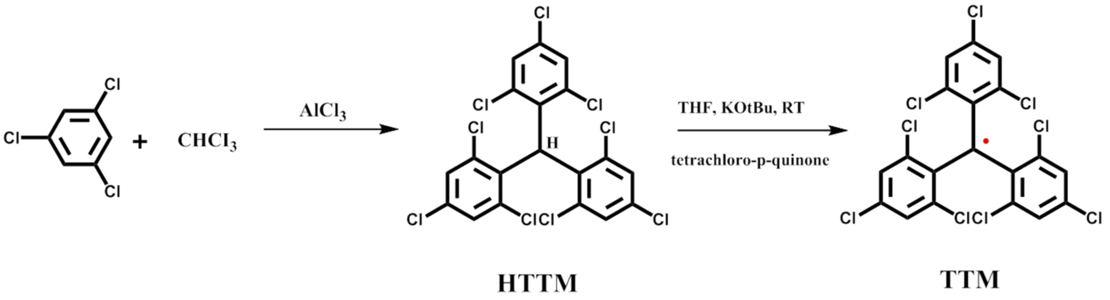


Fig. S1 (a) The raw magnetic susceptibility curve of PS-CzTTM. (b) The raw magnetic susceptibility curve with fit using Curie-Weiss law. (c) The raw magnetic susceptibility curve with fit using equation (1). (d) The corrected magnetic susceptibility curve fitting by Curie-Weiss law.

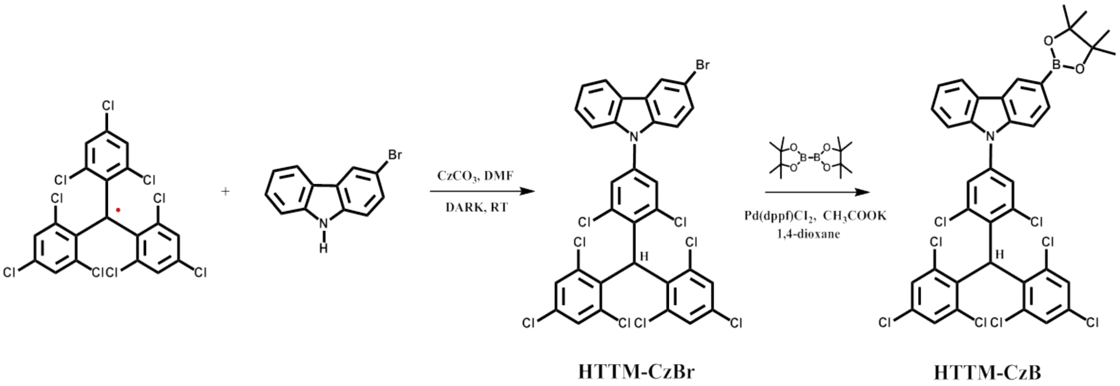
Photostability of radicals was tested under irradiation with a 355 nm pulse laser (power density: 61.4 kW/cm^2, pulse width: 8 ns, frequence: 10 Hz).

1.2 Synthetic procedures and characterization data

Materials synthesis



Tris(2,4,6-trichlorophenyl)methyl (HTTM) and tris(2,4,6-trichlorophenyl)methyl Radical (TTM) were prepared according to our previous reporte[1].

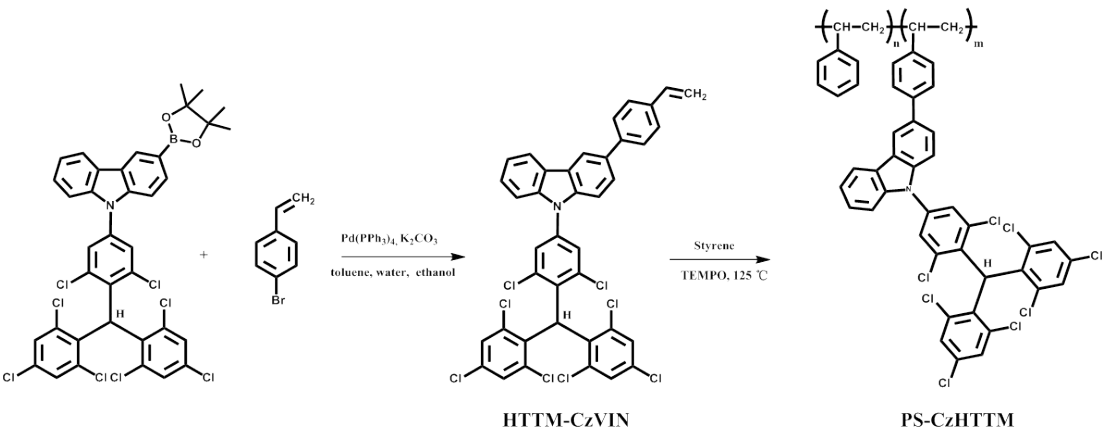


[2,6-Dichloro-4-(3-bromo-N-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl **(HTTM-CzBr)**

A mixture of TTM (3.5 g, 6.33 mmol), 3-Bromo- 9H-carbazole (3.89 g, 15.82mmol), anhydrous CS_2CO_3 (3.30 g, 10.12 mmol) and DMF (40 ml) in a 100 ml round-bottom flask were stirred at 160°C for 6 h under argon atmosphere and in the dark. After the reaction mixture cooling to room temperature, the resulting mixture as poured into (2 M) hydrochloric acid solution, and the precipitate was filtered and washed with water three times. The crude product was dissolved in dichloromethane and further extracted with water and dichloromethane. The organic layer was dried over $MgSO_4$, and evaporated under vacuum. The purification of the crude product by column chromatography (dichloromethane: petroleum =1:5), giving the desired compound HTTM-CzBr as a light red solid (1.2 g, 25%) . ^{1}H NMR (500 MHz, $CDCl_2$) δ 8.30 (s, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 2.1 Hz, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.54 – 7.47 (m, 5H), 7.37 (dd, J = 10.0, 3.8 Hz, 4H), 6.91 (s, 1H). MALID-TOF (m/z):[M] calcd for $C_{31}H_{14}BrC_{l8}N$, 763.96; found, 762.71.

[2,6-Dichloro-4-(3-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-N-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl **(HTTM-CzB)**

HTTM-CzBr (1 g,1.31 mmol), bis(pinacolato)diboron (0.497 g, 1.96 mmol), KOAc (0.768 g, 7.84 mmol) were mixed in a 250 ml round-bottom flask containing 1,4-dioxane （80 ml）. The reaction mixture was stirred at 85℃ for 48 h under argon atmosphere. After the reaction mixture cooling to room temperature, the resulting mixture poured into 100 ml water and extracted with dichloromethane and dried over anhydrous $MgSO_4$. The purification of the crude product by column chromatography (dichloromethane: petroleum =1:3), giving the desired compound HTTM-CzBr as a light brown glassy solid (0.45 g, 42.5%). ^1H NMR (500 MHz, $CDCl_2$) δ 8.63 (s, 1H), 8.22 (d, J = 7.7 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 2.2 Hz, 1H), 7.55 (d, J = 2.2 Hz, 1H), 7.53 – 7.46 (m, 5H), 7.42 – 7.34 (m, 3H), 6.92 (s, 1H), 1.42 (s, 12H). MALID-TOF (m/z):[M] calcd for $C_{31}H_{14}BrC_{l8}N$, 811.03; found, 811.93

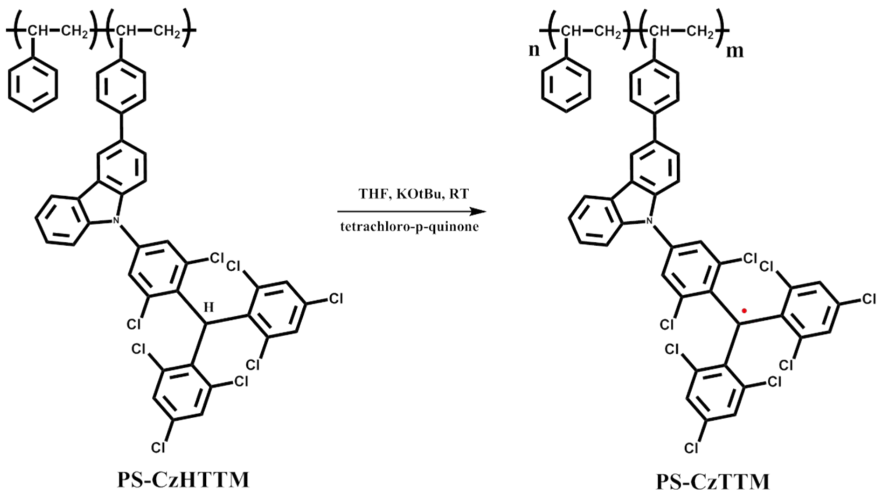


[2,6-Dichloro-4-(4-vinylphenyl)-N-carbazolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl **(HTTM-CzVIN)**

HTTM-CzB（0.4 g, 0.493 mmol）, 1-Bromo-4-vinylbenzene (0.135 g, 0.739 mmol) and Pd(ppd$_3$)$_4$ (0.028g, 0.025 mmol) were mixed in a 100 ml round-bottom flask containing toluene (24 ml), K_2CO_3 aqueous solution (16 ml, 2M), and ethanol (8 ml), the mixture was refluxed at 95°C for 36 h under argon atmosphere. After the reaction mixture cooling to room temperature, the reaction mixture was extracted with dichloromethane. The organic extracts were dried over anhydrous $MgSO_4$. The crude product was further purified by silica gel column chromatography (dichloromethane: petroleum =1:3) to obtain **HTTM-Cz**VIN as green glassy solid (0.35 g, 89%). MALID-TOF (m/z):[M] calcd for $C_{31}H_{14}BrCl_8N$, 787.21; found, 786.79**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 1.4 Hz, 1H), 8.20 (d, J = 7.7 Hz, 1H), 7.74 – 7.70 (m, 3H), 7.66 (d, J = 2.2 Hz, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.49 (d, J = 2.5 Hz, 2H), 7.46 (d, J = 2.2 Hz, 1H), 7.44 (d, J = 2.2 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.34 (d, J = 2.2 Hz, 1H), 7.31 (d, J = 2.2 Hz, 1H), 6.90 (s, 1H), 6.82 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 10.2 Hz, 1H). Elem. Anal. Calcd for $C_{39}H_{21}Cl_8N$, C 59.51, H 2.69, N 1.78; found, C 59.34, H 2.51, N 1.74.

PS-CzHTTM

Under argon atmosphere, TEMPO (6 mg) and styrene (1 ml) were mixed in a 25 ml Schlenk flask, and the mixture was stirred at 120°C for four hours. Then HTTM-CzVIN (60 mg) dissolved in styrene (0.2 ml) was added dropwise and the mixture was stirred at 120°C for 12 h. After the reaction mixture cooling to room temperature, the polymerization was stopped by addition of 10 ml chloroform. The resulting mixture was slowly added in methanol and the precipitate was filtered and washed with methanol repeatedly. In order to completely eliminate the unreacted HTTM-CzVIN, the obtain polymer was extracted with methanol for 36 h by Soxhlet apparatus. In the end, the white polymer PS-CzHTTM was obtained (0.50 g). GPC: M_w=3.87×10^4, M_w=3.44 ×10^4, PDI=1.2.



PS-CzTTM

Under argon atmosphere and in the dark, the KOtBu (2.0 eq.) was added to the solution of PS-CzHTTM (1.0 eq.) in dry THF and the solution acquired a light red colour. The solution was stirred for 5 h at room temperature, and then the tetrachloro-pbenzoquinone (3.0 eq.) was added. The solution was stirred for another 2 h. after the reaction finished, the solvent was removed under vacuum. Next, the crude product was dissolved in chloroform and added in cold methanol and stirred 24 h. Then, the precipitate was filtered and washed with methanol several times. In the end, the light green radical polymer PS-CzTTM was obtained. GPC: M_w=3.87×10^4, M_n=3.44 ×10^4, PDI=1.12. Elem. Anal. C 92.35404, H 7.004957, N 0.170406

MALDI-TOF mass spectra of materials

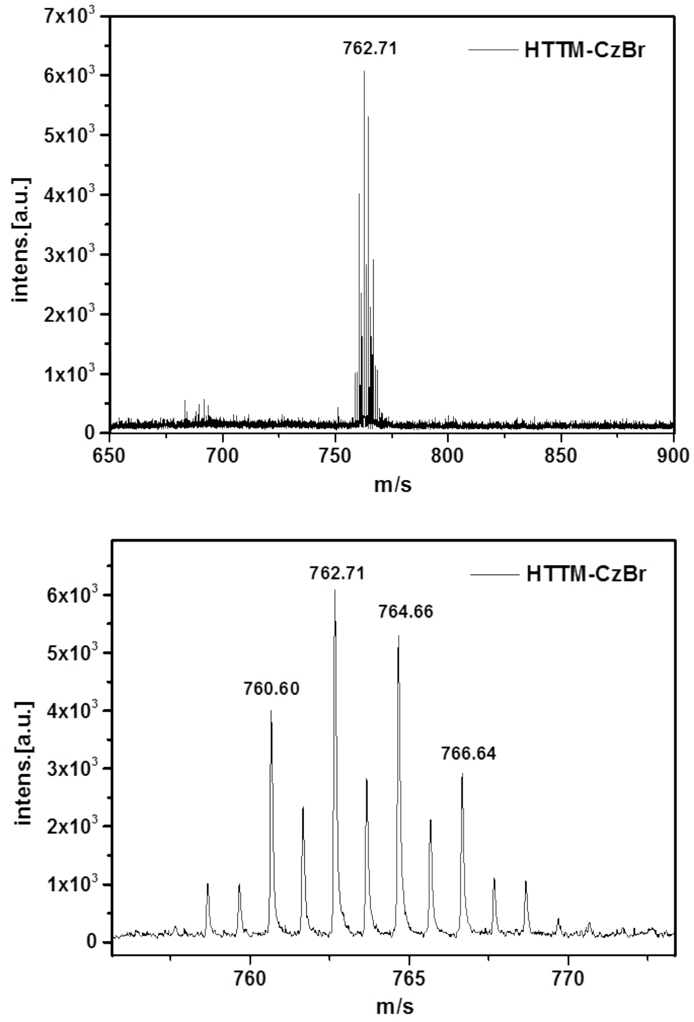


Fig. S2 MALDI-TOF mass spectrum of HTTM-CzBr.

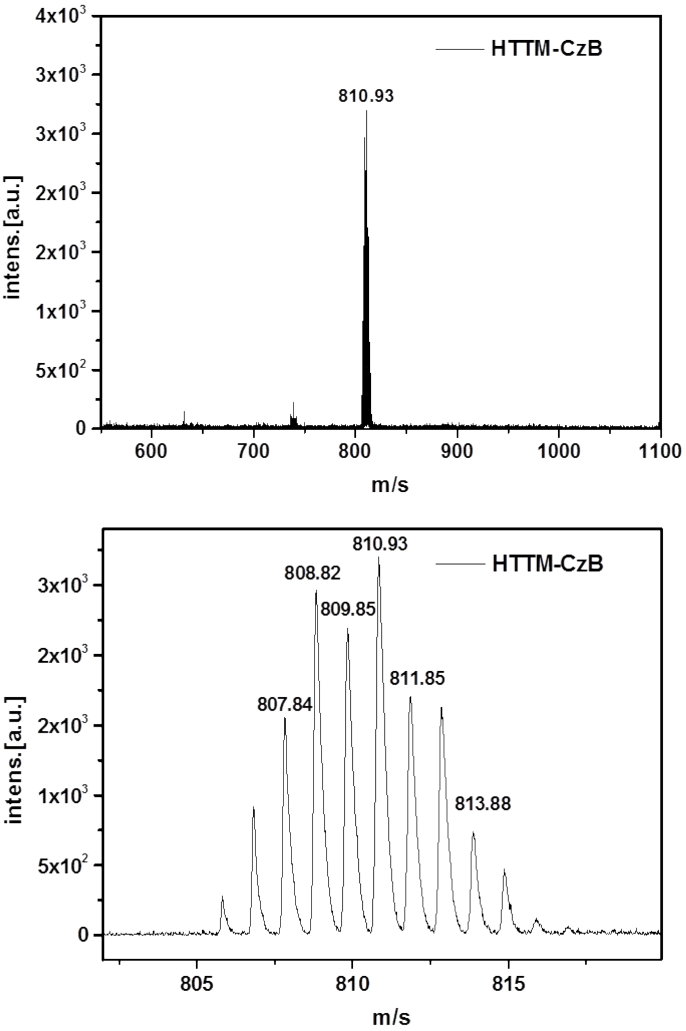


Fig. S3 MALDI-TOF mass spectrum of HTTM-CzB.

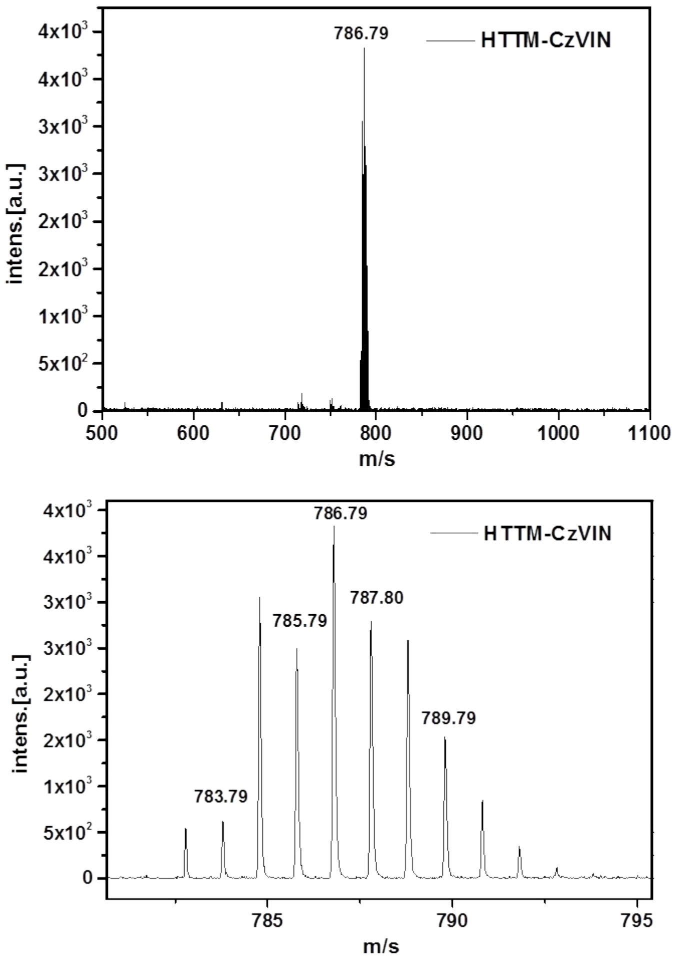


Fig. S4 MALDI-TOF mass spectrum of HTTM-CzVIN.

^{1}H NMR spectra of HTTM-CzBr, HTTM-CzB, HTTM-CzVIN and PS-CzHTTM

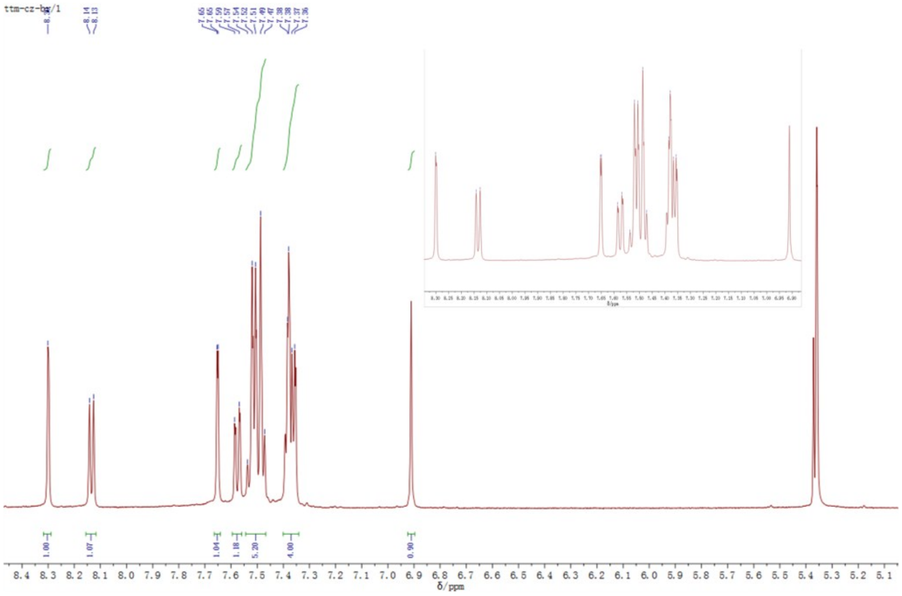


Fig. S5 ^{1}H NMR spectra of HTTM-CzBr in CH_2Cl_2

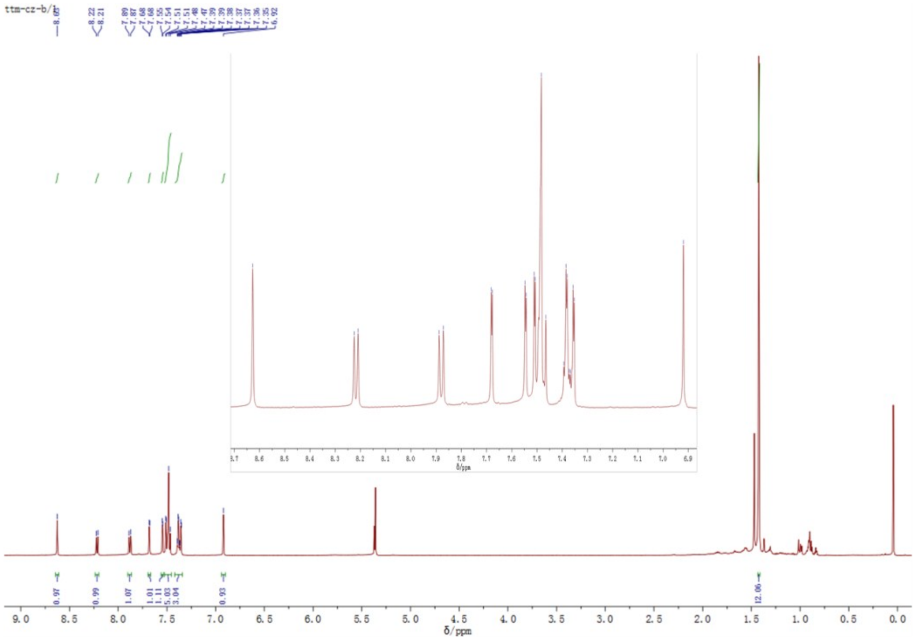


Fig. S6 ^{1}H NMR spectra of HTTM-CzB in CH_2Cl_2

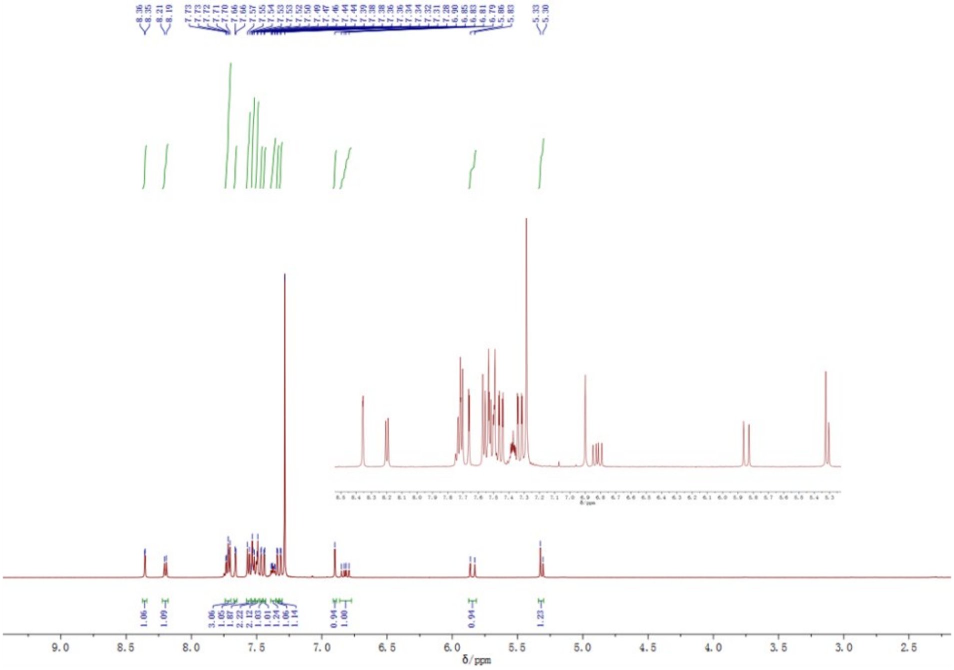


Fig. S7 ^{1}H NMR spectra of HTTM-CzVIN in $CHCl_3$

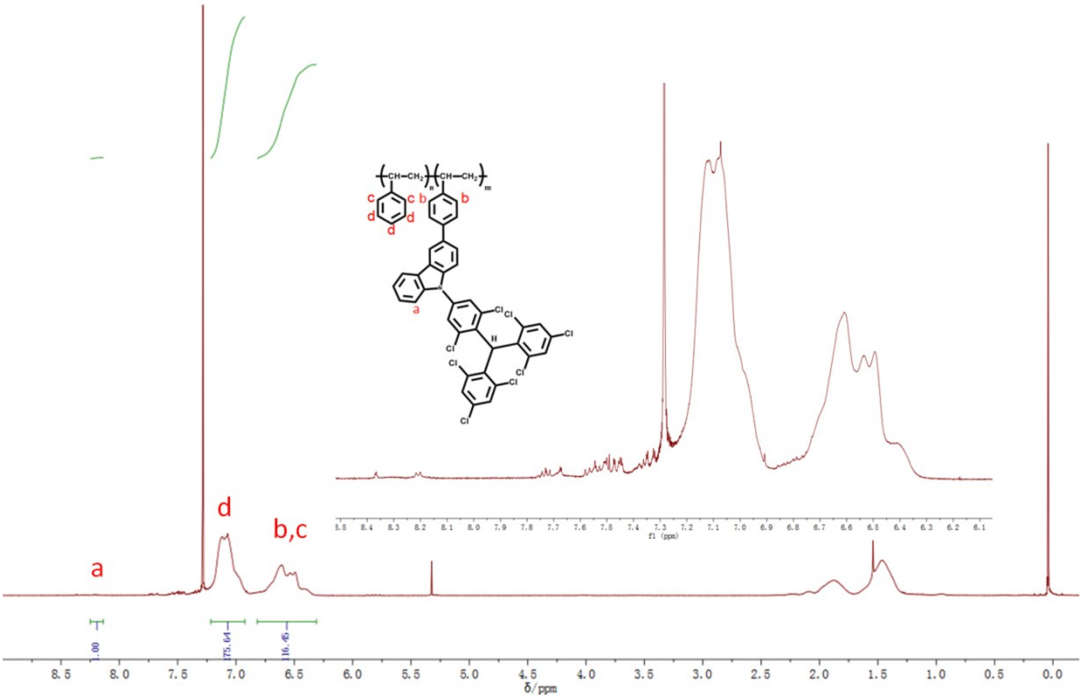


Fig. S8 ^{1}H NMR spectra of PS-CzHTTM in $CHCl_3$

Determination of the number of radical pendants in per chain in the PS-CzTTM

We determined the amount of radical pendant groups (X) in PS-CzTTM via the ^{1}H NMR spectrum of PS-CzHTTM and elemental nalysis data of PS-CzTTM.

Table S1. Elemental analysis data of PS-CzTTM

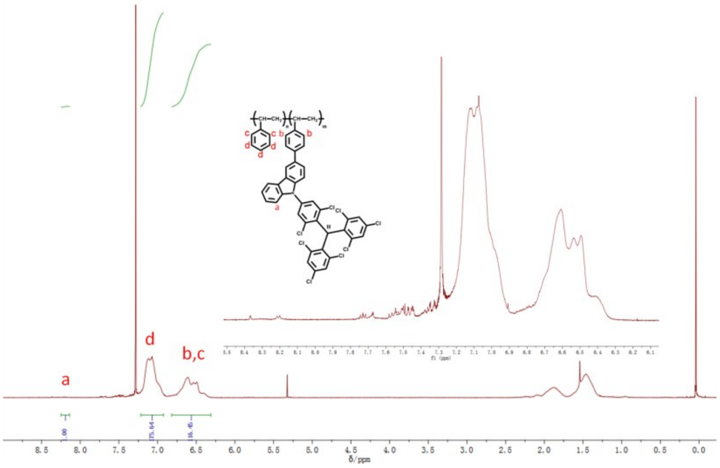
Element name	N%	C%	H%
Content (%)	0.170406	92.35404	7.004957

1. Radical pendant groups (X) was estimated by analyzing the nitrogen content of nitrogen in the elemental analysis data

the amount of radical pendant groups (X) = nitrogen content (N%) × molecular weight (Mw)/14

Accordingly， X≈ 5.

2. The amount of each unit's (n and m) in PS-CzHTTM was estimated by ^{1}H NMR spectra of PS-CzHTTM.



a: d: (b+c)= m : 3n: (2n+2m) =1: 175: 116

Accordingly, n/m = 59

$m \times 787 + n \times 120 = M_w$

Accordingly, n ≈ 292, m ≈ 5, respectively.

Where, 787 and 120 are the molecular weight of the HTTM-CzVIN and styryl unit, respectively.

Through the above two results, we deduced that there are approximately 5 radical pendants in per polymer chain, approximately.

2.UV-Vis-NIR Absorption spectra of PS-CzTTM spin-coated film

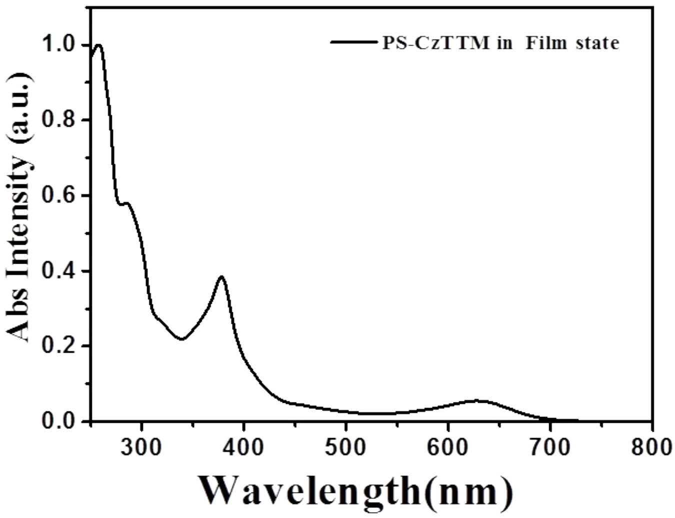


Fig. S9 UV-Vis-NIR Absorption spectra of PS-CzTTM spin-coated film (100 nm).

3.Transient photoluminescence decay spectra

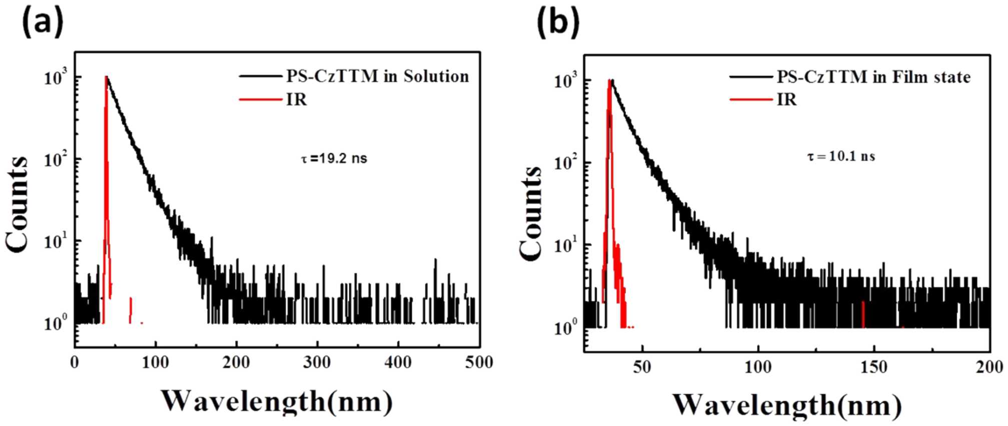


Fig. S10 Transient photoluminescence decay spectra of PS-CzTTM in cychlohexane solution (a) and spin-coated film (b) at room temperature.

4. Electrochemical properties of PS-CzTTM.

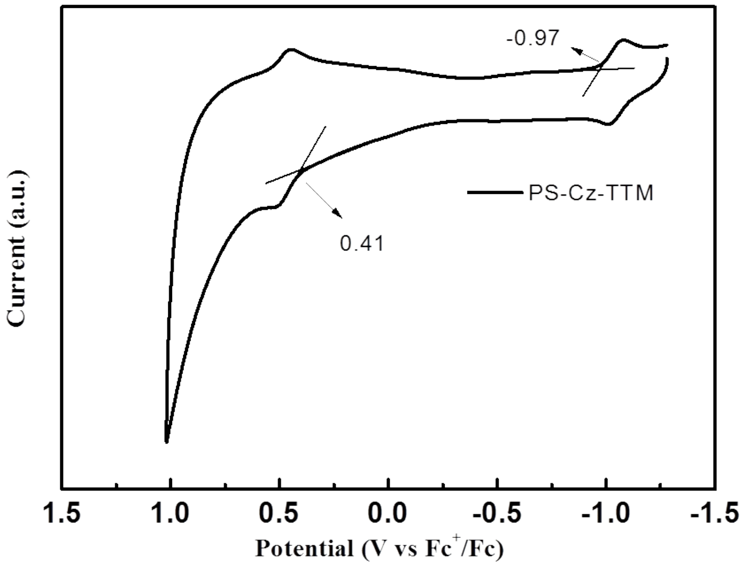


Fig. S11 Cyclic voltammograms of PS-CzTTM in 0.1 M TBAPF$_6$-CH$_2$Cl$_2$ at a scan rate of 0.05 Vs^{-1}. The SOMO and SUMO energy level of PS-CzTTM were calculated to be 5.21 eV (E= (4.8+ (0.41)) eV) and 3.83 eV (E= (4.8+ (-0.97)) eV), respectively.

6. References

1. Q. Peng, A. Obolda, M. Zhang and F. Li, *Angewandte Chemie International Edition*, 2015, **54**, 7091-7095.