Electronic Supplementary Information (ESI) for

Ultrastrong dipole moment induced metal-free organic dyes exhibiting near-infrared (> 800 nm) mechanoresponsive luminescence turn-on

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1. Experimental section

1.1 Materials and characterization

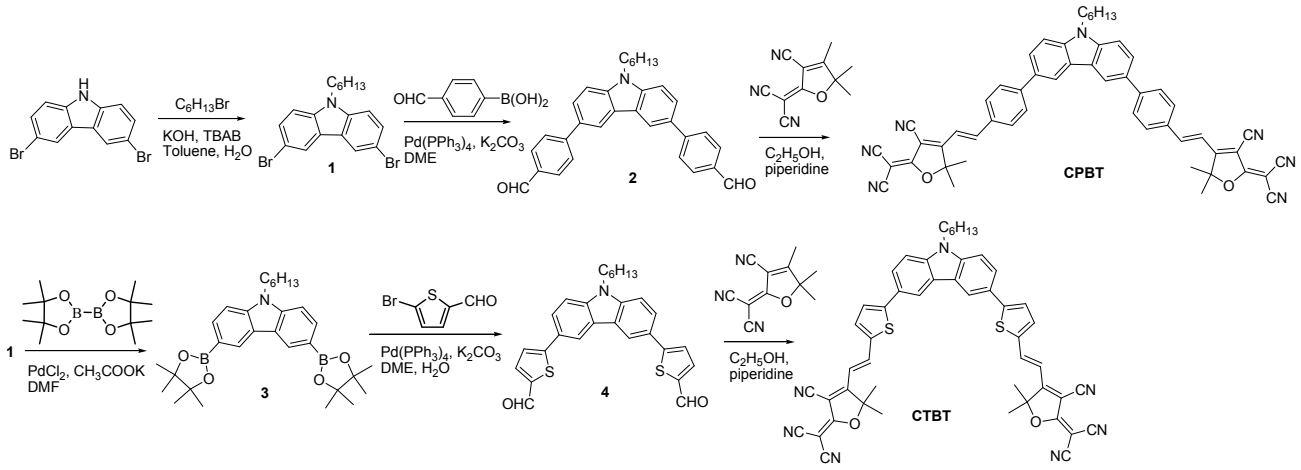
All reagents and solvents were purchased from J&K Chemical and used without purification. NMR spectra measurements were carried out at a Bruker NMR 600 or 400 spectrometer. MALDI-TOF mass spectra were measured on a Waters MALDI Micro MX mass spectrometer with 2,5-dihydroxy benzoic acid (DHB) as the matrix. Elemental analysis was run on a Vario EL III Elemental Analyzer. UV-Vis spectra were recorded on a HTIACH U-3900 Spectrometer. Photoluminescent (PL) spectra were recorded on a HORIBA FluoroMax-4 spectrometer. The absolute fluorescence quantum yields of the compounds in solutions and the solids were measured on a HORIBA FluoroMax-4 spectrometer using an integrating sphere. The transient photoluminescence decay profiles of the solids were recorded using an Edinburgh Instrument FLS980 spectrometer equipped with an EPL-375 picosecond pulsed diode laser. Cyclic voltammetry was performed using a CHI660E analyzer with a scan rate of 100 mV/s in THF solution at room temperature. A platinum plate as the working electrode, a Pt-wire counter electrode, and a saturated calomel electrode (SCE) as the reference electrode were used. The

supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected as the internal standard. Differential scanning calorimetry (DSC) experiments were conducted using a NETZSCH DSC 204 instrument at a scanning rate of 10 K min^{-1}. Powder X-ray diffraction measurements were performed on a Bruker X-ray diffractometer.

1.2 Density functional theory (DFT) calculation

The molecular geometry optimization was carried out using Gaussian 03W package. The results were obtained by DFT calculation using B3LYP functional and the aug-cc-pVTZ basis set in vacuum or with a PCM solvation model. The molecular geometry and orbitals were visualized using Gaussview.

1.3 Synthetic procedures



Scheme S1 Synthetic route for **CPBT** and **CTBT**.

Precursors 3,6-dibromo-9-hexyl-9*H*-carbazole **(1)**, 3,6-bis(4-formylphenyl)-9-hexyl-9*H*-carbazole **(2)** and 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) were prepared according to the previously reported procedure.[S1,S2]

3,6-Bis(2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofurane-1-yl-4-vinylphenyl)-9-hexyl-9*H*-carbazole (CPBT). Compound **2** (918 mg, 2 mmol) was dissolved in absolute ethanol (40

mL) and tetrahydrofuran (10 mL), and stirred at 40 °C for 30 min. Then TCF (877 mg, 4.4 mmol) and piperidine (0.1 mL) were added to the solution. After stirring the solution for an additional 8 h, the precipitate was filtered and dried. The crude product was recrystallized from ethyl ether to afford **CPBT** as a purplish red solid (510 mg, 31%).^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (s, 2H), 8.19 (d, *J* = 8.3 Hz, 4H), 8.00 (d, *J* = 8 Hz, 2H), 7.91 (d, *J* = 4.0 Hz, 2H), 7.84 (d, *J* = 4.0 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 4H), 6.79 (d, *J* = 4.8 Hz, 2H), 4.50-4.47 (m, 2H), 1.81 (s, 12H), 1.29-1.25 (m, 8H), 0.82 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.77, 175.94, 147.87, 145.09, 141.26, 138.54, 133.04, 131.13, 131.00, 129.54, 127.74, 123.40, 115.31, 113.42, 112.18, 110.54, 99.85, 99.13, 54.53, 31.58, 29.07, 26.62, 25.62, 22.51, 14.25. MS (MALDI-TOF, m/z): 821.56 $[M]^+$, 756.66 $[M\text{-}C_3N_2]^+$. Calcd for $C_{54}H_{43}N_7O_2$: C, 78.91; H, 5.27; N, 11.93; O, 3.89. Found: C, 78.73; H, 5.21; N, 11.77.

3,6-Bis(4,4,5,5-tetamethyl-1,3,2-dioxaborolan-2-yl)-9-hexyl-carbazole (3). A mixture of **1** (4.12 g, 10 mmol), bis(pinacolato)diboron (8 g, 32 mmol), $PdCl_2$ (0.71g, 1.1 mmol), CH_3COOK (2 g, 20 mmol) in DMF was stirred at 110 °C for 24 h. After cooling to room temperature, the mixture was poured into H_2O, extracted with chloroform and dried over anhydrous $MgSO_4$. After filtration and concentration under reduced pressure, the product was obtained as a yellow solid using silica gel column chromatography (ethyl acetate : ethylacetate = 1 : 10 by volume) (11.6 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 7.2 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.37 (s, 24H), 1.36 – 1.28 (m, 6H), 0.84 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.68, 132.00, 128.08, 122.84, 108.16, 83.55, 43.14, 31.59, 28.91, 26.81, 24.97, 22.54, 14.04. MS (MALDI-TOF, m/z): 503.41 $[M]^+$. Calcd for $C_{30}H_{43}B_2NO_4$: C, 71.59; H, 8.61; B, 4.30; N, 2.78; O, 12.72. Found: C, 71.30; H, 8.63; N, 2.73.

3,6-Bis(5-formylthiophene-2-yl)-9-hexyl-9*H*-carbazole (4). A mixture of 5-bromothiophene-2-

carbaldehyde (4.2 g, 22 mmol), **3** (5 g, 10 mmol), $Pd(PPh_3)_4$ (1.11 g, 1 mmol) and K_2CO_3 (13.8 g, 100 mmol) in DME (40 mL) was stirring at 100 °C for 24 h. After cooling to room temperature, the mixture was poured into H_2O and extracted with chloroform. The extracts were washed with H_2O and subsequently dried over anhydrous $MgSO_4$. After filtration and concentration under reduced pressure, compound **4** was afforded by recrystallization from ethanol as a yellow-green solid (7.9 g, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.90 (s, 2H), 8.43 (d, *J* = 1.6 Hz, 2H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.78 (d, *J* = 3.6 Hz, 2H), 7.48 (d, *J* = 4.2 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 7.2 Hz, 2H), 1.89 (m, 2H), 1.36 – 1.20 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.63, 155.67, 141.48, 137.91, 136.97, 126.47, 124.96, 124.75, 123.09, 118.58, 109.72, 43.46, 31.51, 28.96, 26.91, 22.53, 14.02. MS (MALDI-TOF, m/z): 471.20 $[M]^+$. Calcd for $C_{28}H_{25}NO_2S_2$: C, 71.31; H, 5.34; N, 2.97; O, 6.78; S, 13.60. Found: C, 71.25; H, 5.39; N, 2.91.

3,6-Bis(2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofurane-1-yl-4-vinylphenyl)-9-hexyl-carbazole (CTBT). Compound **4** (471 mg, 1 mmol) was dissolved in absolute ethanol (25 mL) and tetrahydrofuran (15 mL), and stirred at 75 °C for 30 min. Then TCF (439 mg, 2.2 mmol) and piperidine (0.1 mL) were added to the solution. After stirring the solution for an additional 7 h, the precipitate was filtered and dried. The crude product was recrystallized from ethyl ether to afford **CTBT** as a black solid (292 g, 35%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.89 (d, *J* = 1.8 Hz, 2H), 8.18 (d, *J* = 15.6 Hz, 2H), 7.99 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.90 (d, *J* = 4.2 Hz, 2H), 7.83 (d, *J* = 4.2 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 15.6 Hz, 2H), 4.47 (t, *J* = 6.6 Hz, 2H), 1.82 (s, 12H), 1.76 (m, 2H), 1.23 (m, 6H), 0.80 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.63, 175.71, 147.77, 145.00, 141.30, 141.21, 136.37, 133.04, 130.82, 127.35, 123.48, 115.15, 113.26, 112.43, 110.71, 110.54, 99.79, 99.25, 54.59, 31.48, 29.07, 26.65, 25.71, 22.52, 14.42. MS (MALDI-TOF, m/z): 833.43

[M]$^{+}$, 651.33 [M-$C_{10}H_6N_3O$]+H^{+}, 1033.21 [M+matrix-CH_3]+H^{+}. Calcd for $C_{50}H_{39}N_7O_2S_2$: C, 72.00; H, 4.71; N, 11.76; O, 3.84; S, 7.69 Found: C, 71.84; H, 4.76; N, 11.72.

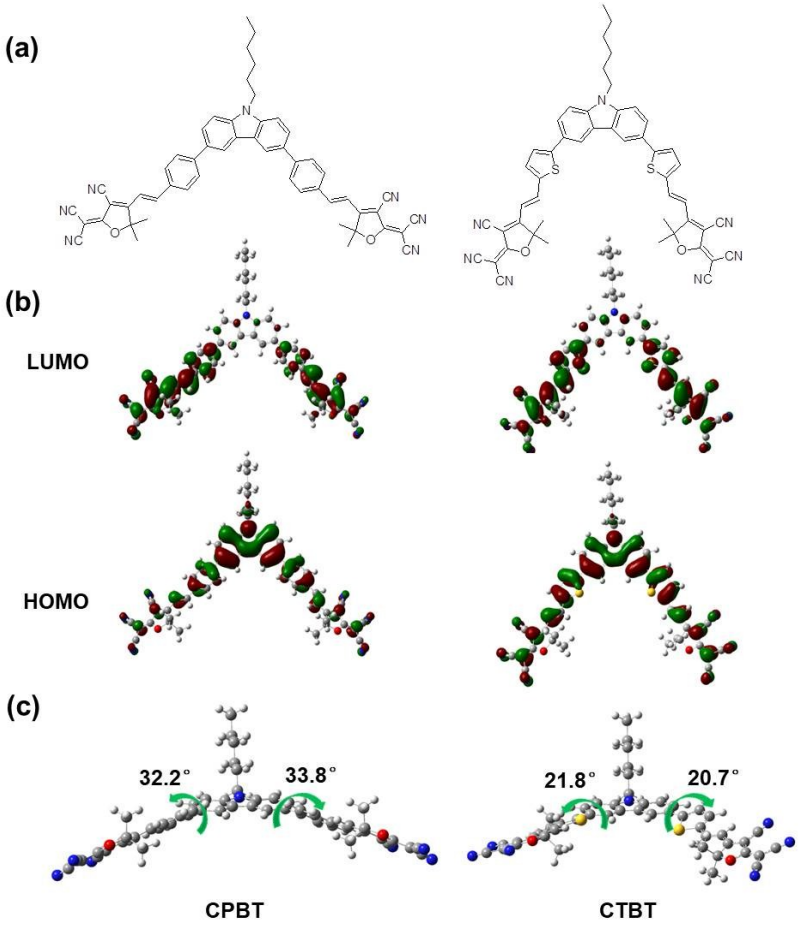


Fig. S1 (a) Molecular structure, (b) geometrically optimized HOMO and LUMO spatial distributions and (c) molecular conformations in THF solution of **CPBT** and **CTBT** obtained via DFT B3LYP/aug-cc-pVTZ calculations.

As the solvent polarity will strongly impact the frontier orbital levels of the molecules with TICT characteristics, to get a more precise prediction on the frontier orbital levels in the testing solution, the energy minimized structures of **CPBT** and **CTBT** were also calculated with a PCM model using THF as the solvent. The twisting angles between the central carbazole and the π-units were 32.2°/33.8° for **CPBT** and 21.8°/20.7° for **CTBT**, respectively (Fig. S1c), which was in accordance with the trends in vacuum. The calculations pointed out that **CTBT** with thienyl π-bridge possessed a flatter skeleton in comparison with **CPBT** which possessed phenyl π-linker.

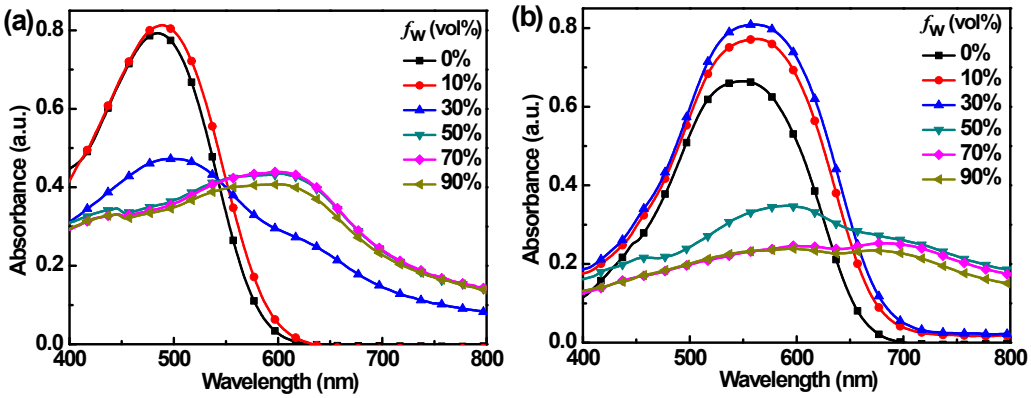


Fig. S2 UV-vis absorption spectra of (a) **CPBT** and (b) **CTBT** in THF/H_2O mixtures with different water fractions (f_ws).

With the increase of the water fractions (f_w), the leveled-off tails of the absorption band clearly appeared in the long-wavelength region ($f_w \geq 30$ vol% for **CPBT**, $f_w \geq 50$ vol% for **CTBT**), indicating the formation of the nano-sized aggregates.

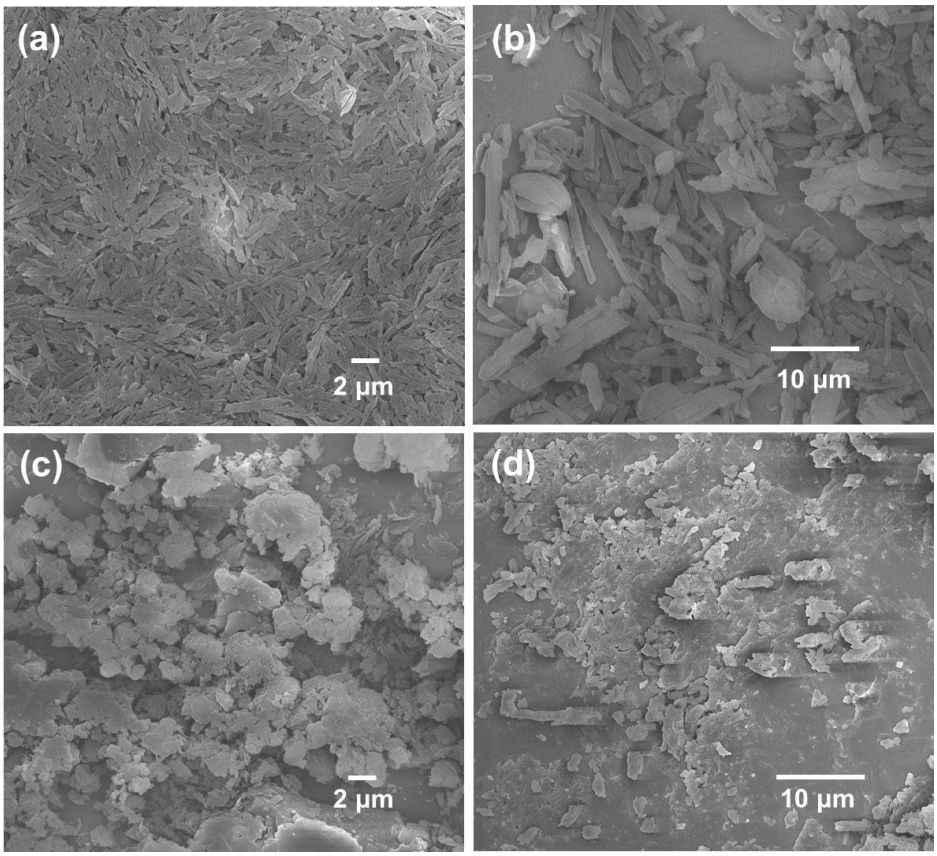


Fig. S3 SEM images of the pristine samples of (a) **CPBT** and (b) **CTBT**, and the ground samples of (c) **CPBT** and (d) **CTBT**.

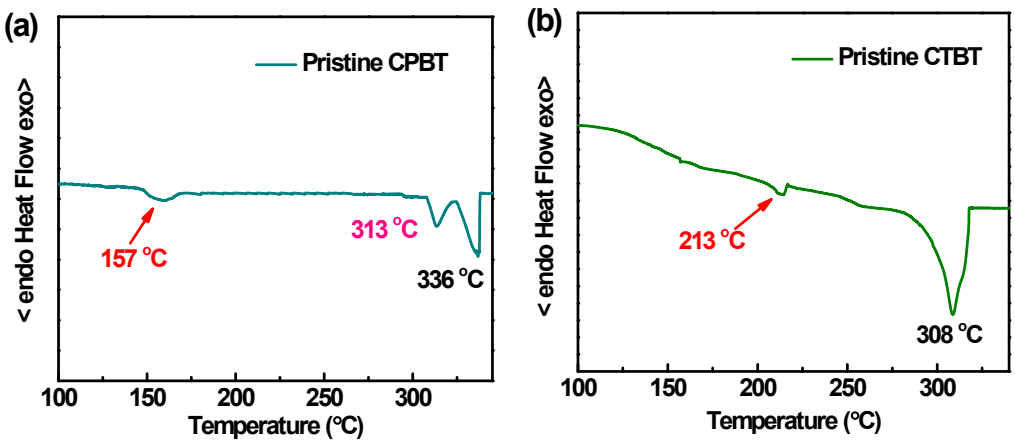


Fig. S4 DSC curves of the pristine samples of (a) **CPBT** and (b) **CTBT**.

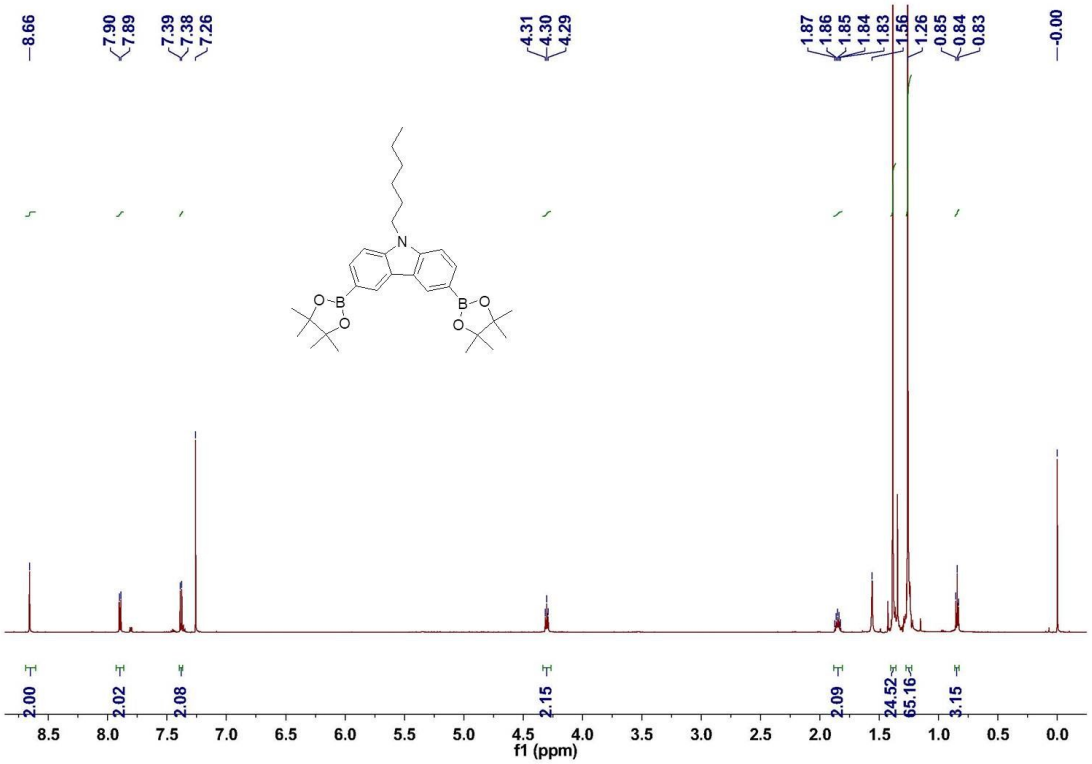


Fig. S5 ^{1}H NMR spectrum of compound **3**.

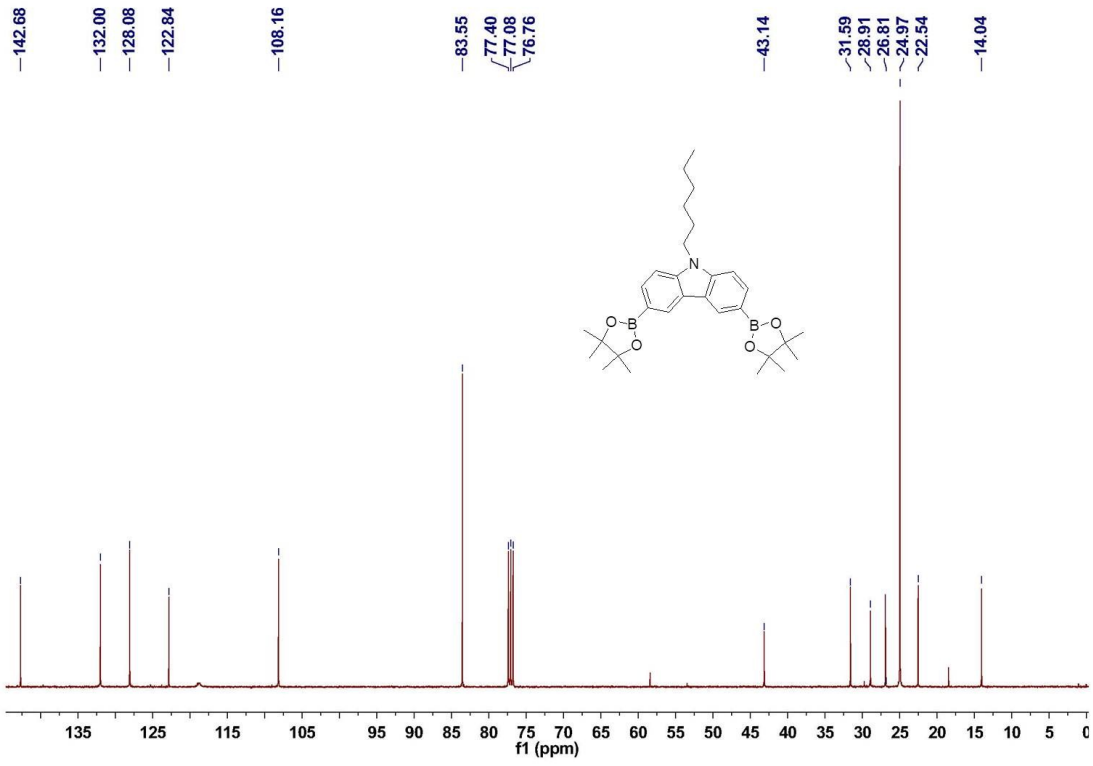


Fig. S6 ^{13}C NMR spectrum of compound **3**.

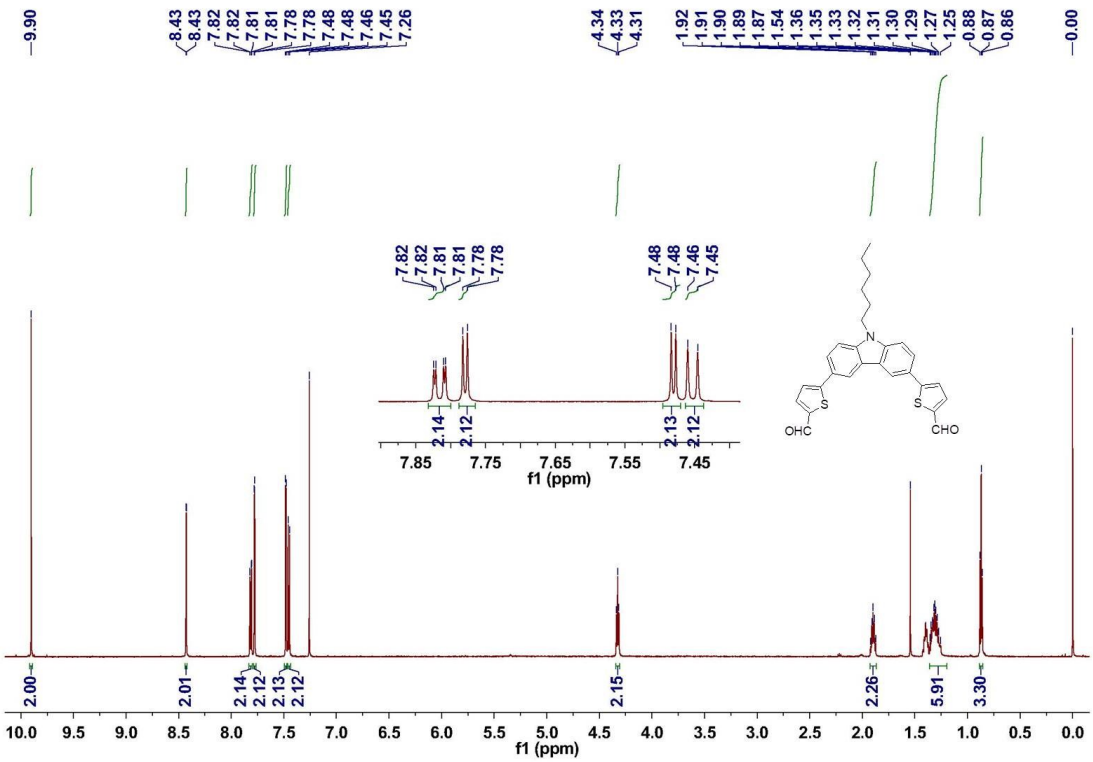


Fig. S7 ^{1}H NMR spectrum of compound **4**.

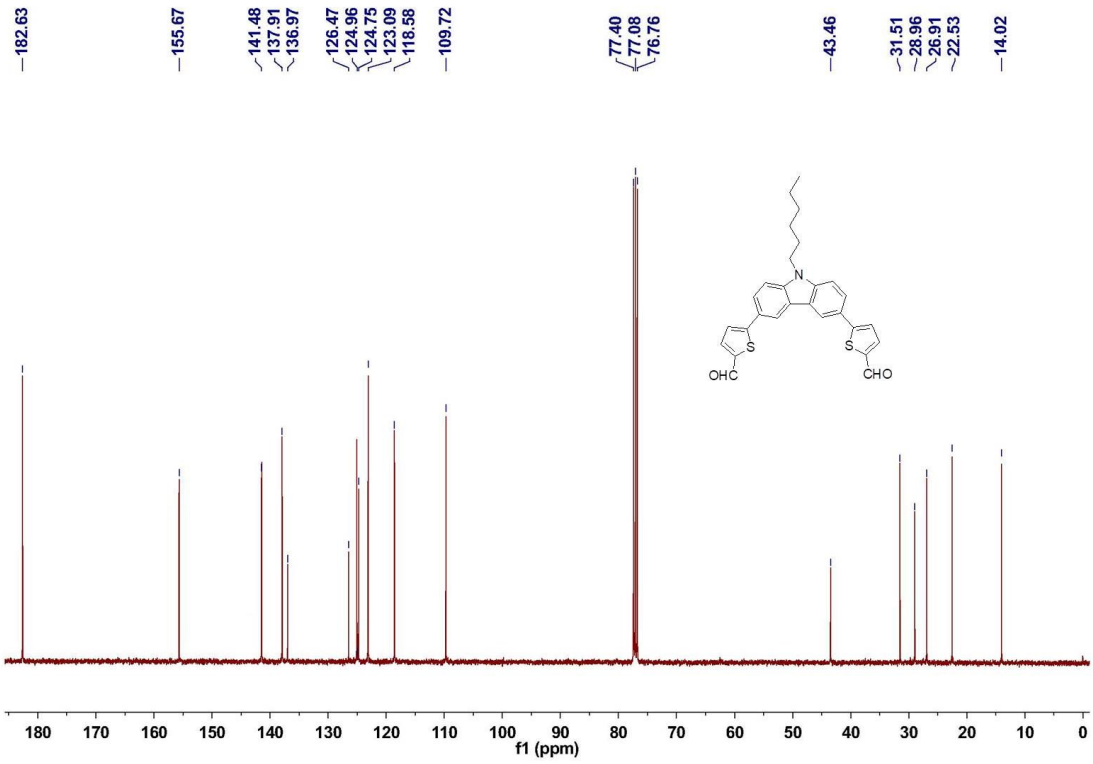


Fig. S8 ^{13}C NMR spectrum of compound **4**.

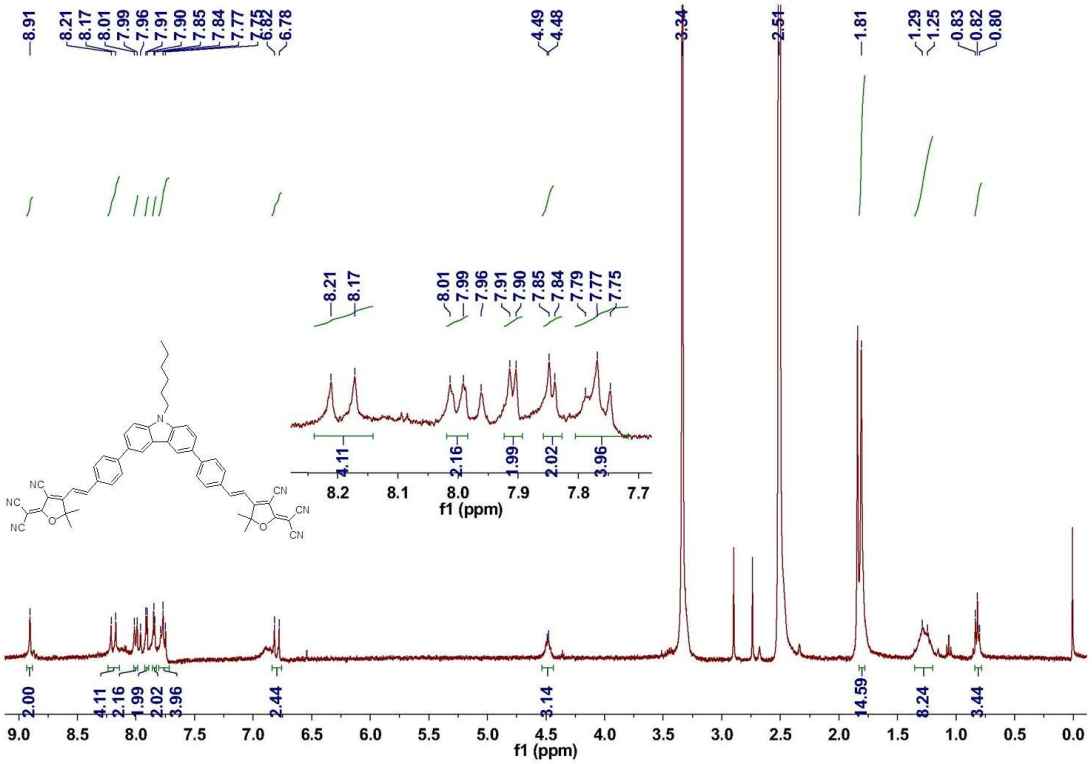


Fig. S9 ^{1}H NMR spectrum of compound **CPBT**.

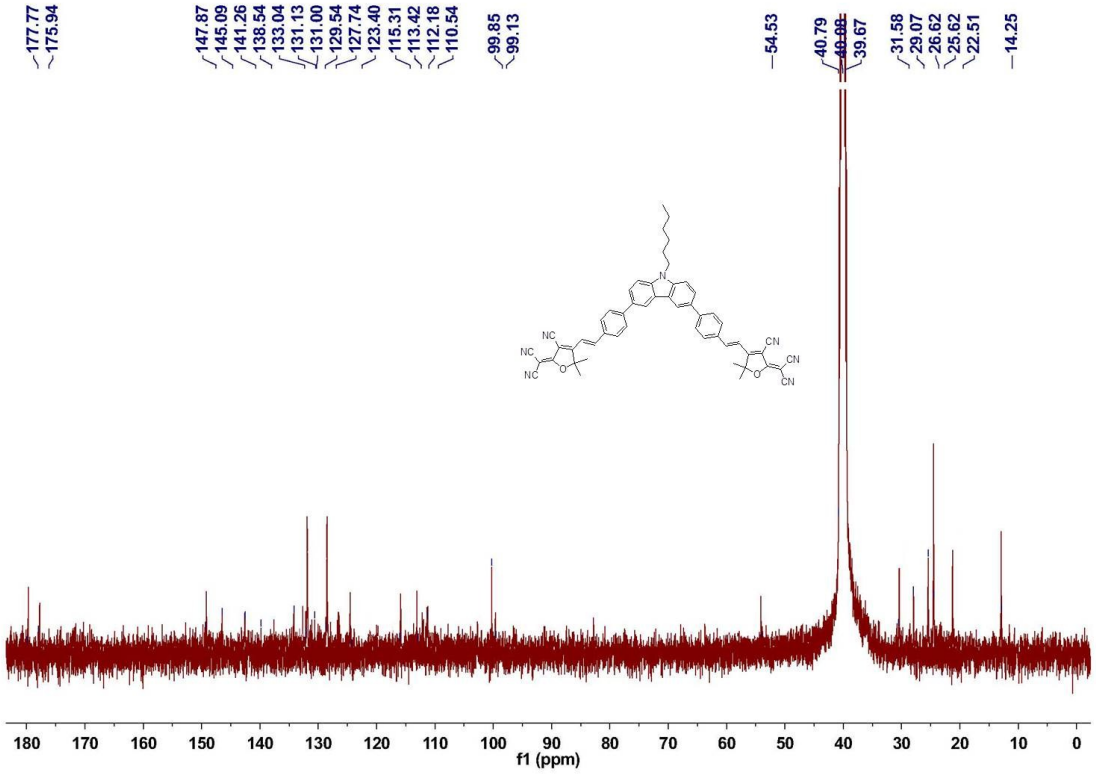


Fig. S10 ^{13}C NMR spectrum of compound **CPBT**.

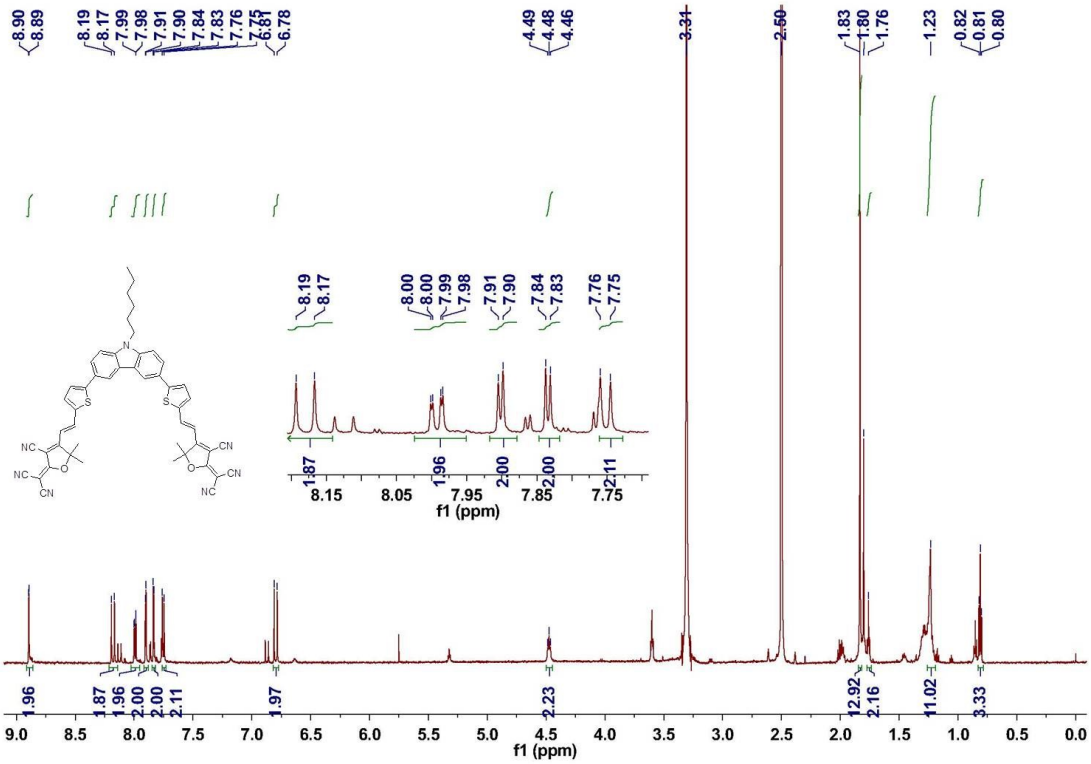


Fig. S11 ^{1}H NMR spectrum of compound **CTBT**.

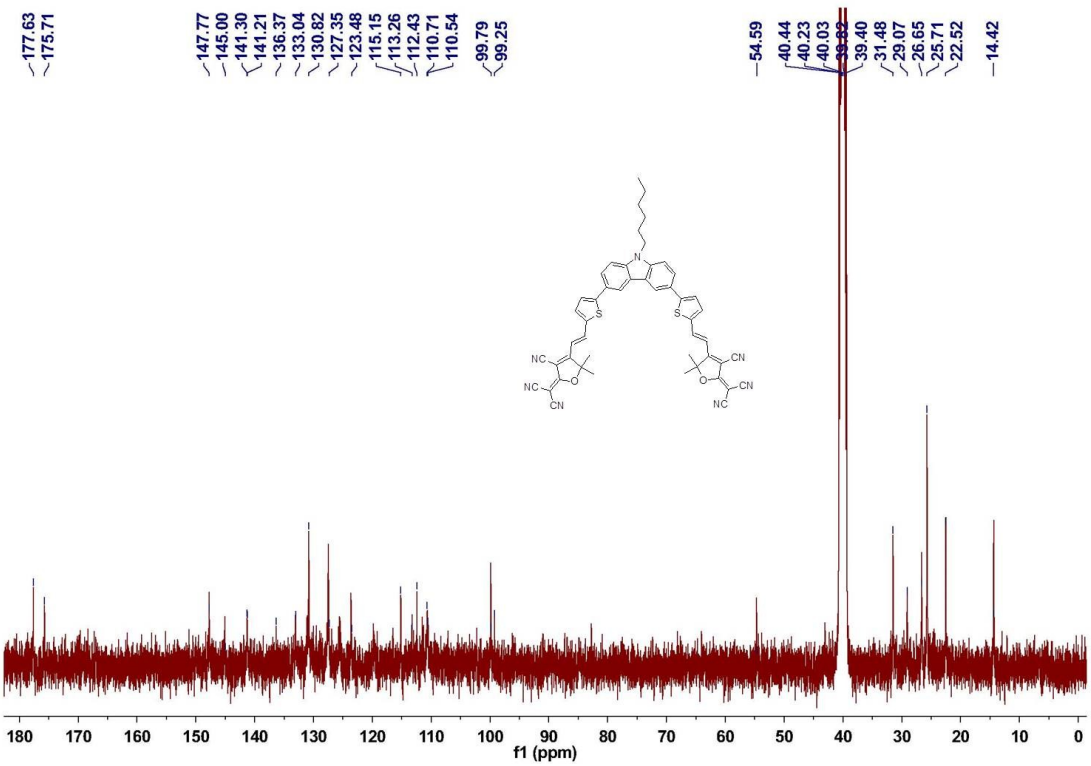


Fig. S12 ^{13}C NMR spectrum of compound **CTBT**.

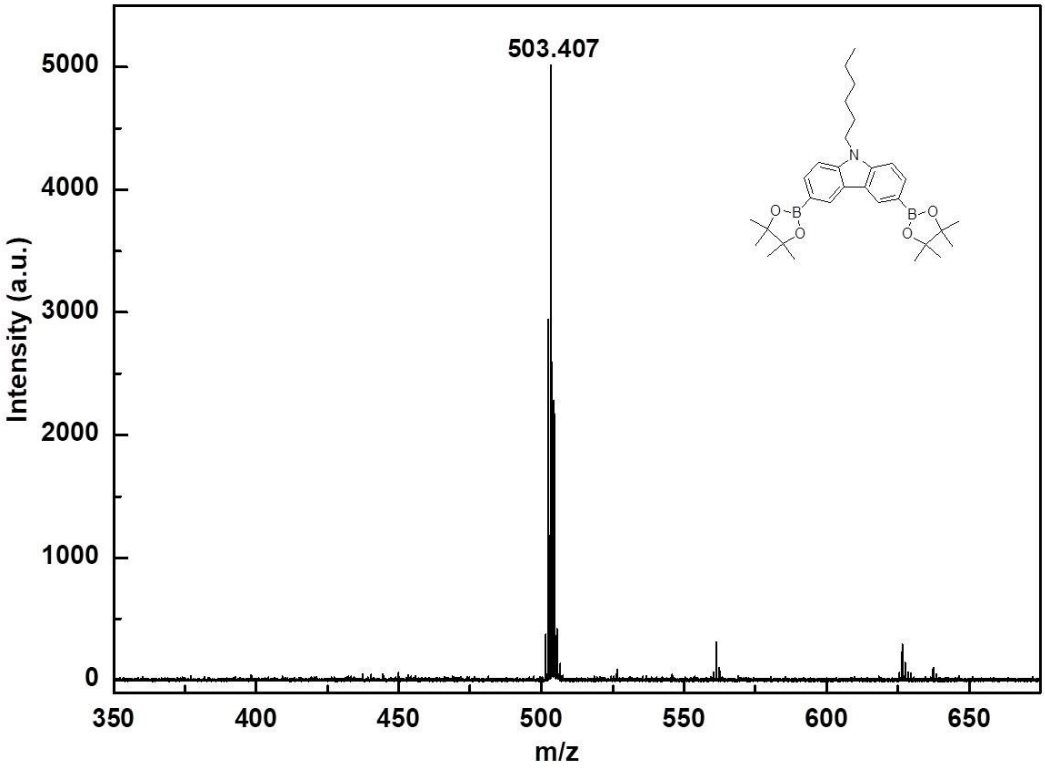


Fig. S13 MS spectrum of compound **3**.

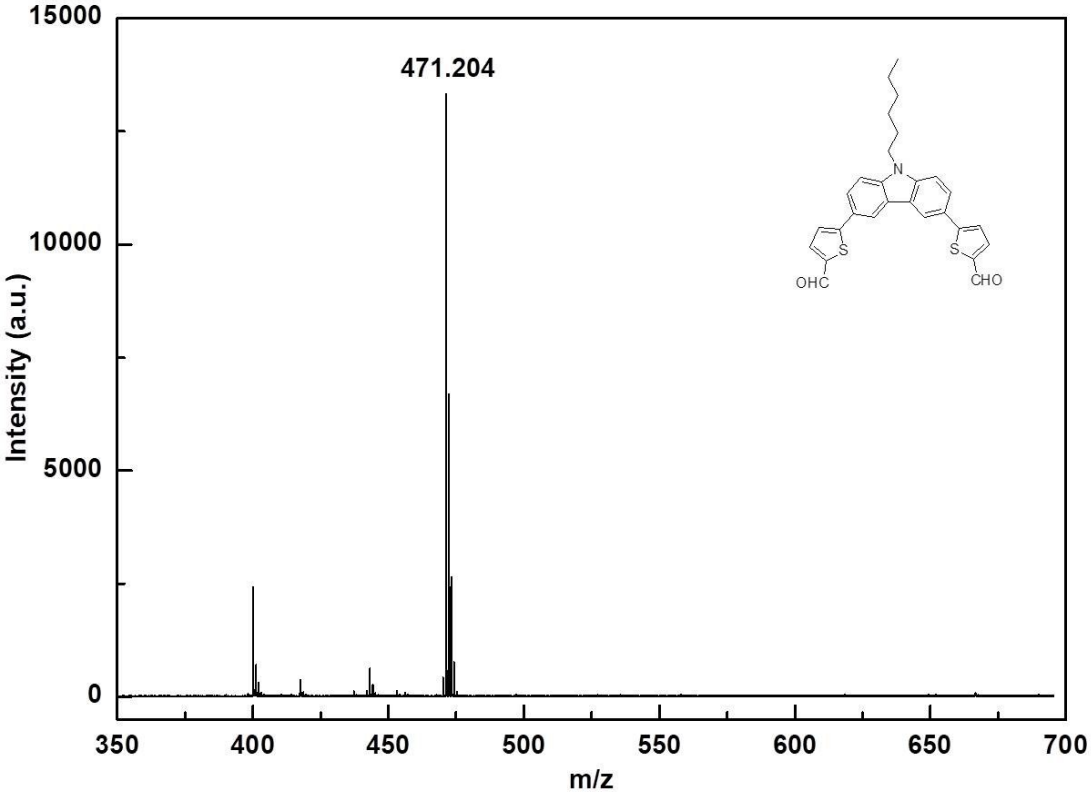


Fig. S14 MS spectrum of compound **4**.

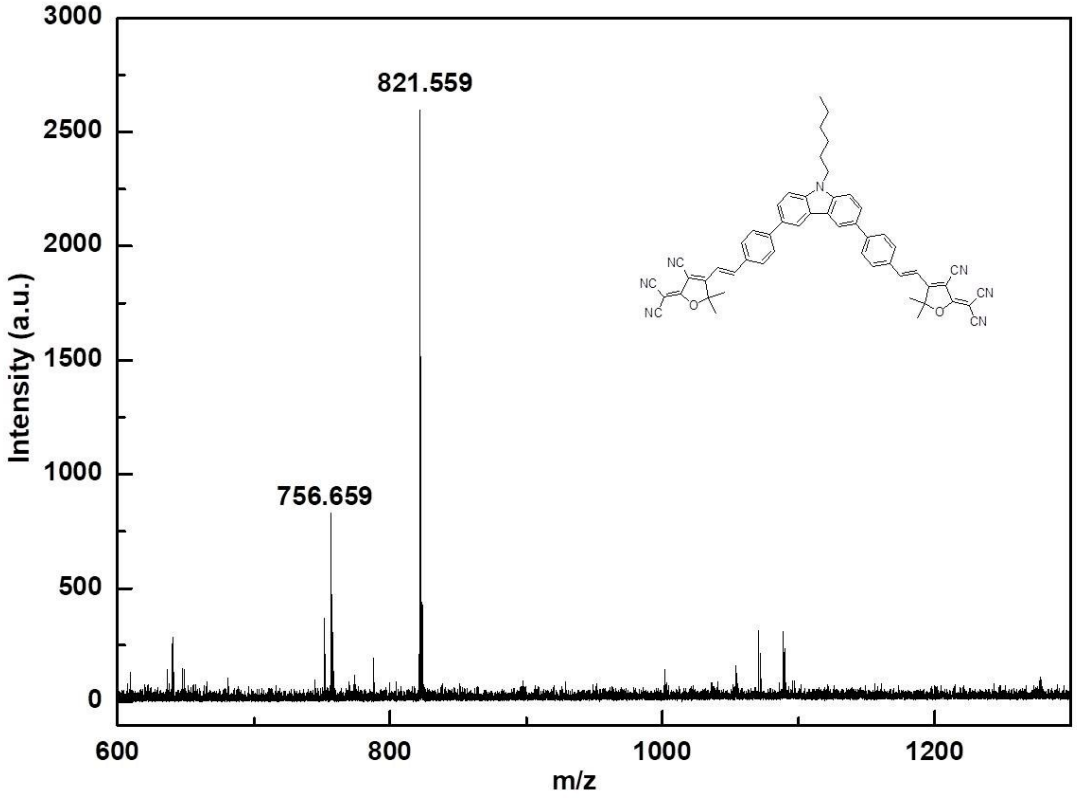


Fig. S15 MS spectrum of compound **CPBT**.

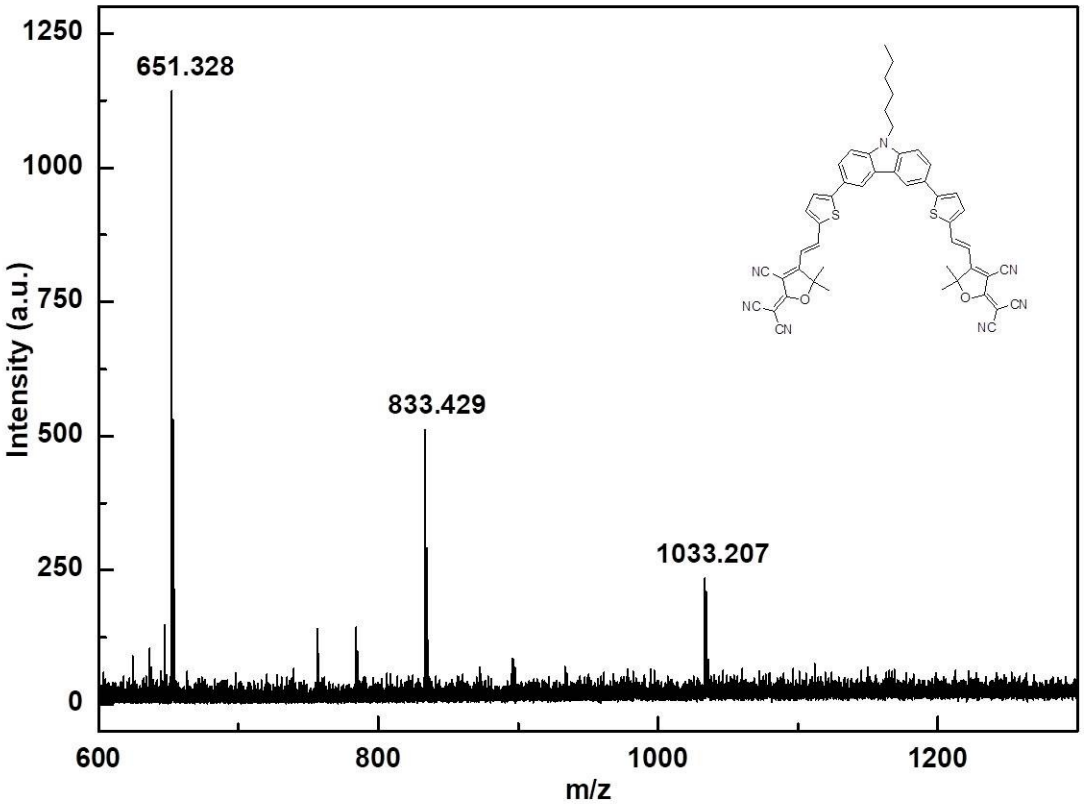


Fig. S16 MS spectrum of compound **CTBT**.

References

S1. P. Wen, Z. Gao, R. Zhang, A. Li, F. Zhang, J. Li, J. Xie, Y. Wu, M. Wu and K. Guo, *J. Mater. Chem. C*, 2017, **5**, 6136-6143.

S2. M.-Y. Wu, K. Li, C.-Y. Li, J.-T. Hou and X.-Q. Yu, *Chem. Commun.*, 2014, **50**, 183-185.