

Electronic Supplementary Information (ESI)

New Thermally Stable Aggregation-Induced Emission Enhancement Compounds for Non-doped Red Organic Light-Emitting Diodes

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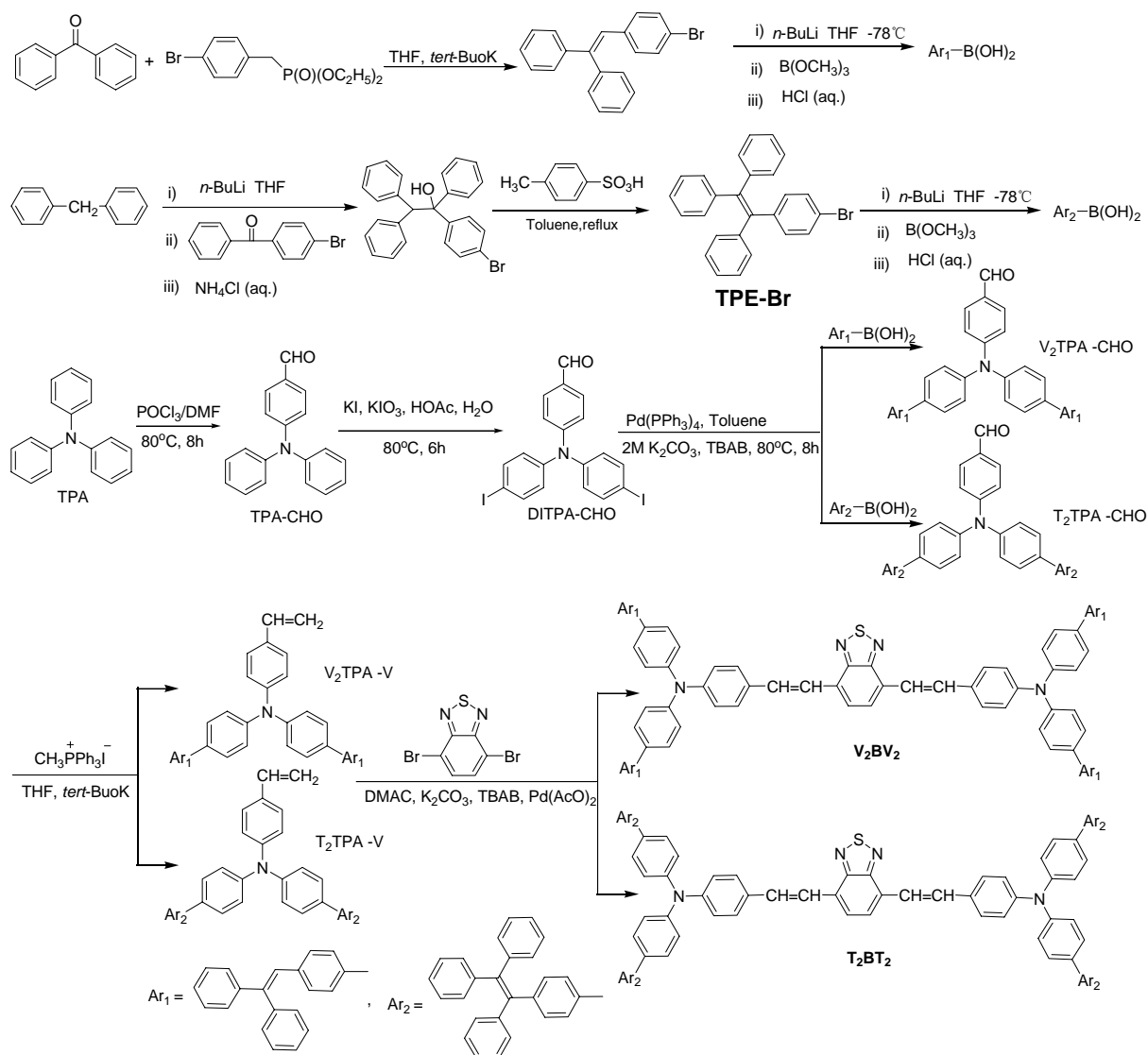
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Materials and Measurements

Diphenylmethane, benzophenone, 4-bromobenzophenone, *n*-butyllithium in hexane (2.2M), 4, 7-dibromobenzo-1, 2, 5-thiadiazole, palladium acetate, tetrabutyl ammonium bromide (TBAB), trimethyl borate, *t*-BuOK, POCl₃, KI, KIO₃ and K₂CO₃ purchased from Alfa Aesar were used as received. Triphenylamine was obtained from Zhenjiang Haitong Chemical Industry Co., Ltd. (China). All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Company (China) and used without further purification. Intermediates **T₂TPA-CHO**¹ and **Ar₁-B(OH)₂**² were prepared according to the literature procedures.

Proton and carbon nuclear magnetic resonance (¹H-NMR and ¹³C-NMR) spectra were measured on Mercury-Plus 300 spectrometer (for intermediates) and Varian INOVA500NB spectrometer (for ¹³C-NMR of the target products) [CDCl₃, tetramethylsilane (TMS) as the internal standard]. Mass spectra (MS) were measured on a VG ZAB-HS Double Focussing Mass Spectrometer or a Thermo DSQ MS spectrometer. Elemental analyses (EA) were performed with an Elementar Vario EL elemental analyzer. Photoluminescence spectra (PL) were measured on a Shimadzu RF-5301pc spectrometer. UV-vis absorption spectra (UV) were recorded on a Hitachi UV-vis spectrophotometer (U-3900). Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204 F1) at a heating rate of 10 °C/min under N₂ atmosphere. Thermogravimetric analyses (TGA) were carried out using a thermal analyzer (Shimadzu, TGA-50H) under N₂ gas flow with a heating rate of 20 °C/min. Cyclic voltammetry (CV) measurement was carried out on a Shanghai Chenhua electrochemical workstations CHI660C in a three-electrode cell with a Pt disk working electrode, a

Ag/AgCl reference electrode, and a glassy carbon counter electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1M tetrabutylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$) in dichloromethane at scan rate of 100 mV/s using ferrocene (Fc) as standard. The HOMO energy levels were obtained using the onset oxidation potentials from the CV curves. The lowest unoccupied molecular orbital/highest occupied molecular orbital (LUMO/HOMO) energy gaps ΔE_g for the compounds were estimated from the onset absorption wavelengths of UV absorption spectra. The water-DMF mixtures with different water fractions were prepared by slowly adding distilled water into the DMF solution of samples under ultrasound at room temperature. For example, a 70% water fraction mixture was prepared in a volumetric flask by adding 7 mL distilled water into 3 mL DMF solution of the sample. The concentrations of all samples were adjusted to 5 μM after adding distilled water.



Scheme S1. Synthetic routes to the compounds.

Synthesis of compound V₂TPA-CHO

DITPA-CHO (1.58g, 3.0 mmol) and Ar₁-B(OH)₂ (1.80g, 6.0 mmol) in toluene (40 mL), 2M aqueous K₂CO₃ solution (9 mL) and TBAB (0.1g) were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the Pd(PPh₃)₄ catalyst (catalytic amount) was added and the reaction mixture was stirred at 80°C for 16 h. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography with CH₂Cl₂: n-hexane (v: v; 2: 3), Light yellow powder of V₂TPA-CHO was obtained in 83% yield. ¹HNMR (300 MHz, CDCl₃) δ(ppm): 7.00 (s, 2H), 7.07-7.12 (dd, 6H), 7.17-7.26 (m, 8H), 7.27-7.40 (m, 20H), 7.46-7.55 (d, 4H), 7.68-7.73 (d, 2H), 9.82 (s, 1H); ¹³CNMR (75MHz, CDCl₃) δ(ppm): 120.35, 126.50, 127.80, 128.20, 128.40, 129.00, 129.80, 130.30, 130.65, 131.60, 136.75, 137.35, 138.40, 140.06, 143.00, 143.50, 145.45, 153.15, 190.50; MS (EI), m/z: 781([M]⁺, calcd for C₅₉H₄₃NO, 781); Anal. Calcd. For C₅₉H₄₃NO: C 90.62, H 5.54, N 1.79, O 2.05; Found: C 90.55, H 5.57, N 1.71.

Synthesis of compound V₂TPA-V and T₂TPA-V

Methyltriphenylphosphonium Iodide (0.88g, 2.2 mmol), and the corresponding aldehyde (2.0 mmol) were solved in anhydrous THF (40 mL). Then the mixtures were stirred under an Argon atmosphere at room temperature. After 30 min, potassium tert-butyloxyde (0.268g, 2.4 mmol) was added and the mixture was stirred for another 4 h. The reaction mixture was concentrated and purified by silica gel column chromatography with CH₂Cl₂: n-hexane (v:v, 1: 5, V₂TPA-V, yield 61%; v:v, 1: 4, T₂TPA-V, yield 53%). V₂TPA-V: ¹HNMR (300 MHz, CDCl₃) δ(ppm): 5.18 (d, 1H), 5.565 (d, 1H), 6.70 (dd, 1H), 7.00 (s, 2H), 7.05-7.15 (m, 10H), 7.20-7.40 (m, 26H), 7.40-7.50 (d, 4H). ¹³CNMR (75MHz, CDCl₃) δ(ppm): 112.70, 124.50, 126.25, 127.40, 127.80, 128.00, 128.40, 129.00, 130.20, 130.60, 132.60, 135.10, 136.25, 138.80, 140.70, 142.70, 143.60, 146.85, 147.20. T₂TPA-V: ¹HNMR (300 MHz, CDCl₃) δ(ppm): 5.17 (d, 1H), 5.65 (d, 1H), 6.67 (dd, 1H), 7.00-7.15 (m, 40H), 7.27-7.35 (m, 6H), 7.45 (d, 4H). ¹³CNMR (75MHz, CDCl₃) δ(ppm): 111.30, 112.65, 124.20, 124.60, 125.90, 126.70, 127.40, 128.00, 131.60, 132.00, 132.45, 135.30, 136.40, 137.00, 137.40, 138.40, 139.50, 140.05, 140.75, 141.20, 142.65, 144.00, 146.80, 147.30, 148.00.

Synthesis of compound V₂BV₂ and T₂BT₂

4, 7-dibromobenzo-1, 2, 5-thiadiazole (0.126g, 0.43 mmol), anhydrous K₂CO₃ (0.61g, 4.5 mmol), 0.1g TBAB, and the corresponding vinyltriphenylamine derivative (0.90 mmol) were solved in anhydrous DMAc (30 mL). The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the Pd(OAc)₂ catalyst (catalytic amount) was added

and the reaction mixture was stirred at 120°C for 24 h. After cooling to room temperature, the reaction mixture was concentrated and purified by silica gel column chromatography with CH₂Cl₂: n-hexane (v:v, 1: 4, V₂BV₂, yield 33%; v:v, 1: 3, T₂BT₂, yield 26%).

V₂BV₂: ¹HNMR(300 MHz, CDCl₃) δ(ppm): 7.00 (s, 4H), 7.05-7.20 (m, 20H), 7.23-7.40 (m, 48H), 7.43-7.58 (m, 14H), 7.62-7.67 (s, 2H), 7.90-7.98 (d, 2H); ¹³CNMR(125 MHz, CDCl₃)δ(ppm): 123.11, 123.83, 124.65, 126.08, 126.57, 127.60, 128.23, 128.74, 129.29, 130.03, 130.42, 131.85, 132.13, 132.44, 135.29, 136.17, 138.58, 140.50, 142.59, 143.45, 146.53, 147.39, 153.67, 154.00; MS (FAB), m/z: 1691([M]⁺, calcd for C₁₂₆H₉₀N₄S 1691).

T₂BT₂: ¹HNMR(300 MHz, CDCl₃) δ(ppm): 7.00-7.20 (m, 79H), 7.30-7.40 (d, 9H), 7.43-7.57 (m, 14H), 7.63 (s, 2H), 7.95 (s, 2H). ¹³CNMR(125 MHz, CDCl₃) δ(ppm): 123.40, 123.65, 124.68, 125.73, 126.48, 127.64, 127.76, 129.27, 131.36, 131.42, 131.83, 132.01, 132.43, 135.39, 138.13, 140.60, 141.10, 142.50, 143.79, 146.46, 147.42, 154.00. MS (FAB), m/z: 1995([M]⁺, calcd for C₁₅₀H₁₀₆N₄S 1995).

References

1. H. Li, Z. Chi, B. Xu, X. Zhang, X. Li, S. Liu, Y. Zhang, J. Xu, *J. Mater. Chem.* 2011, **21**, 3760.
2. S. Wang, W. J. Oldham Jr, R. A. Hudack Jr, G. C. Bazan, *J. Am. Chem. Soc.* 2000, **122**, 5695.

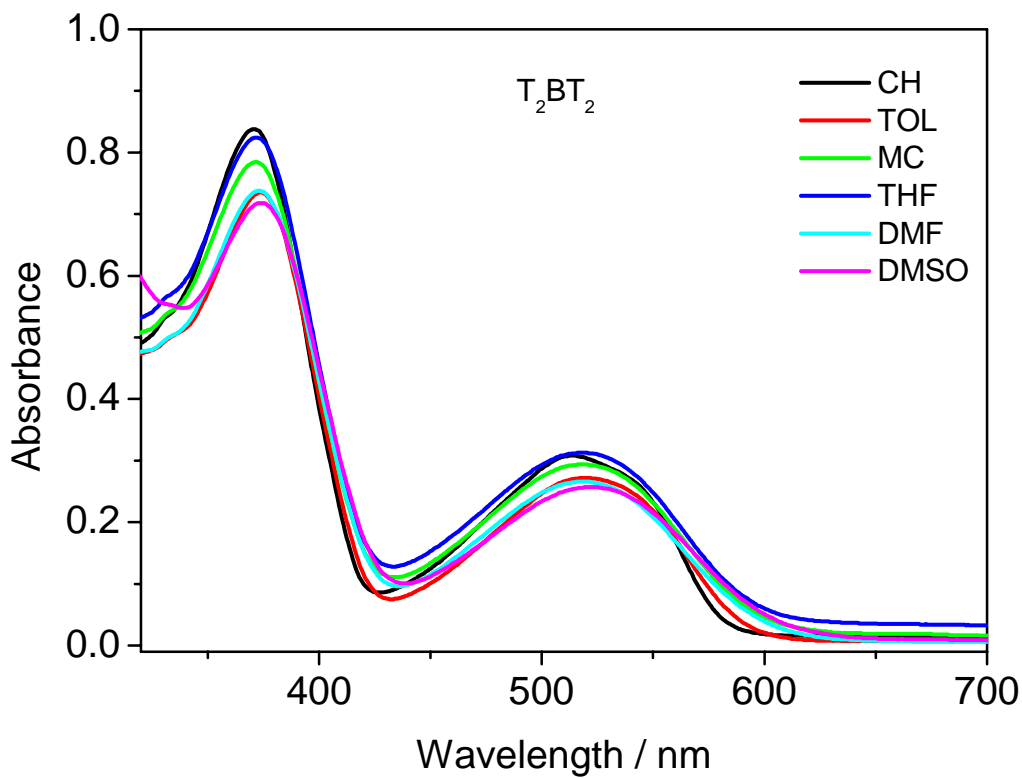
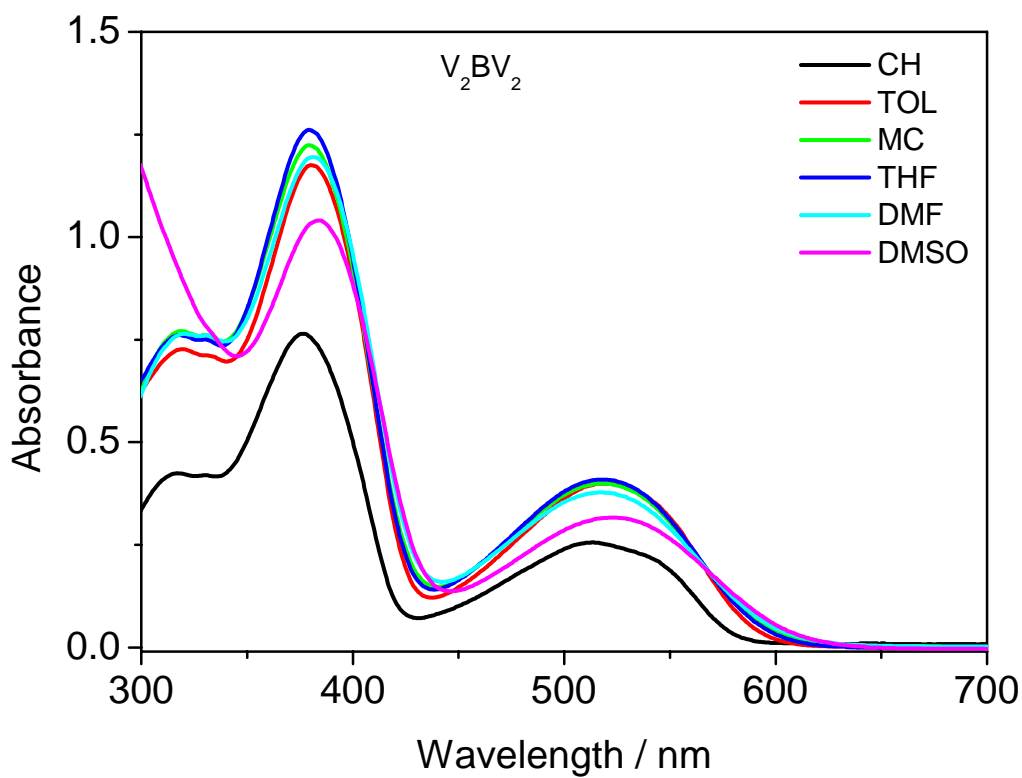


Fig. S1. UV-vis absorption spectra of V_2BV_2 and T_2BT_2 in different solvents (5 μ M).

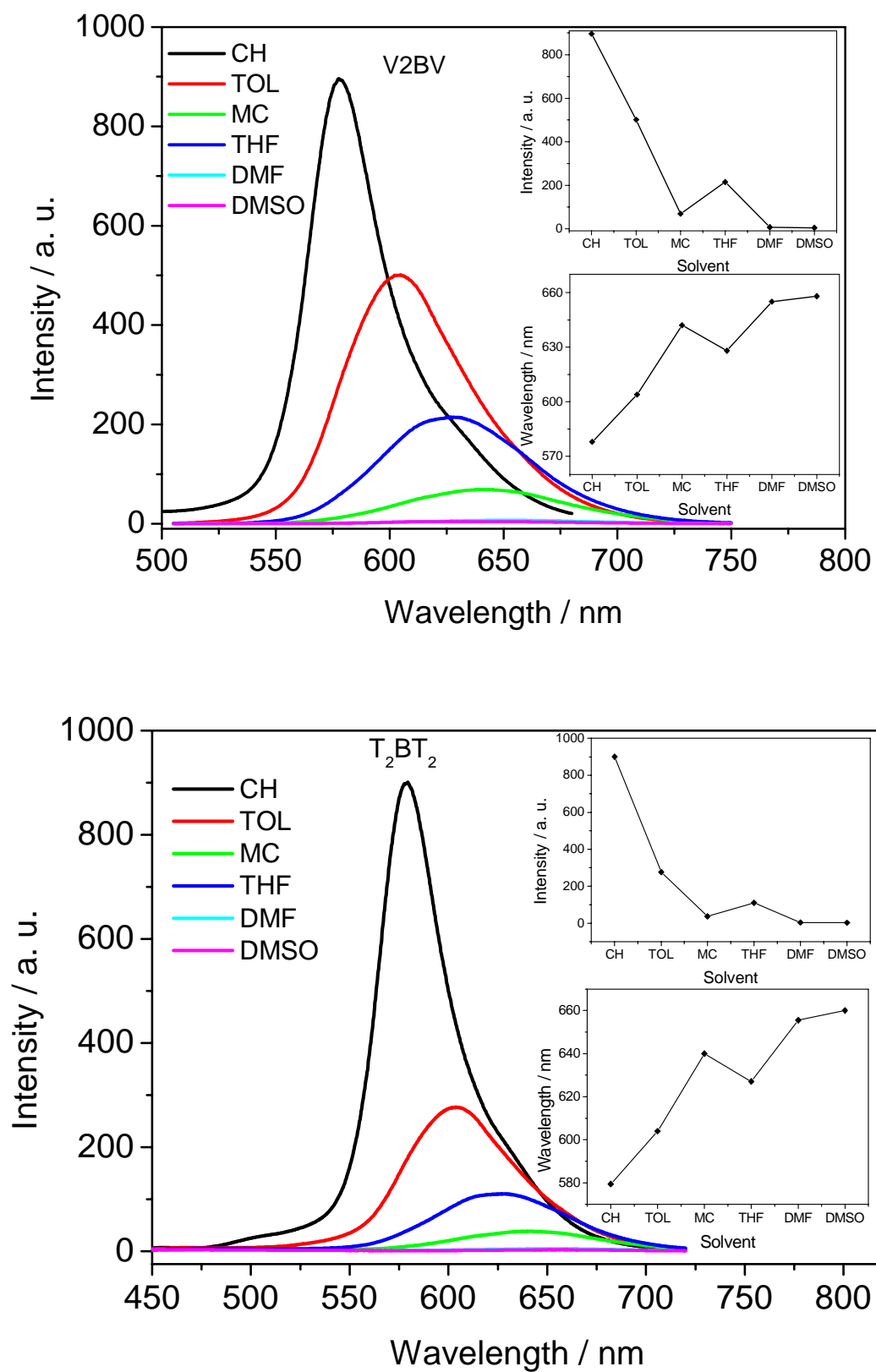


Fig. S2. PL emission spectra of V₂BV₂ and T₂BT₂ in different solvents (5 μM).

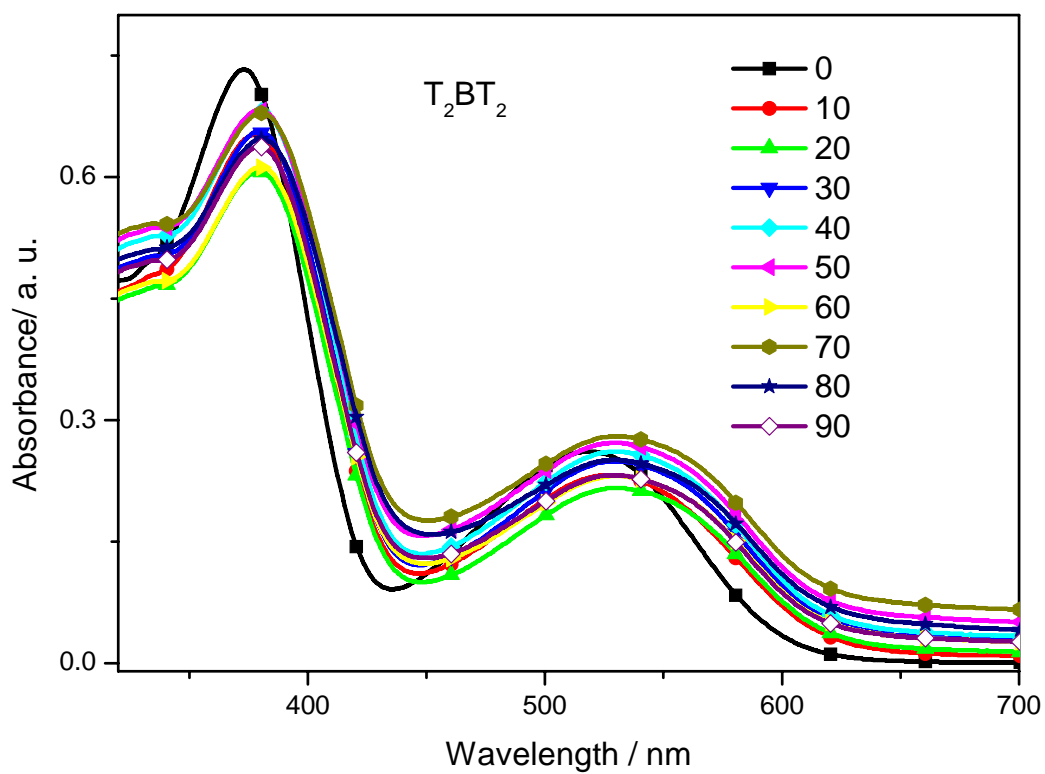
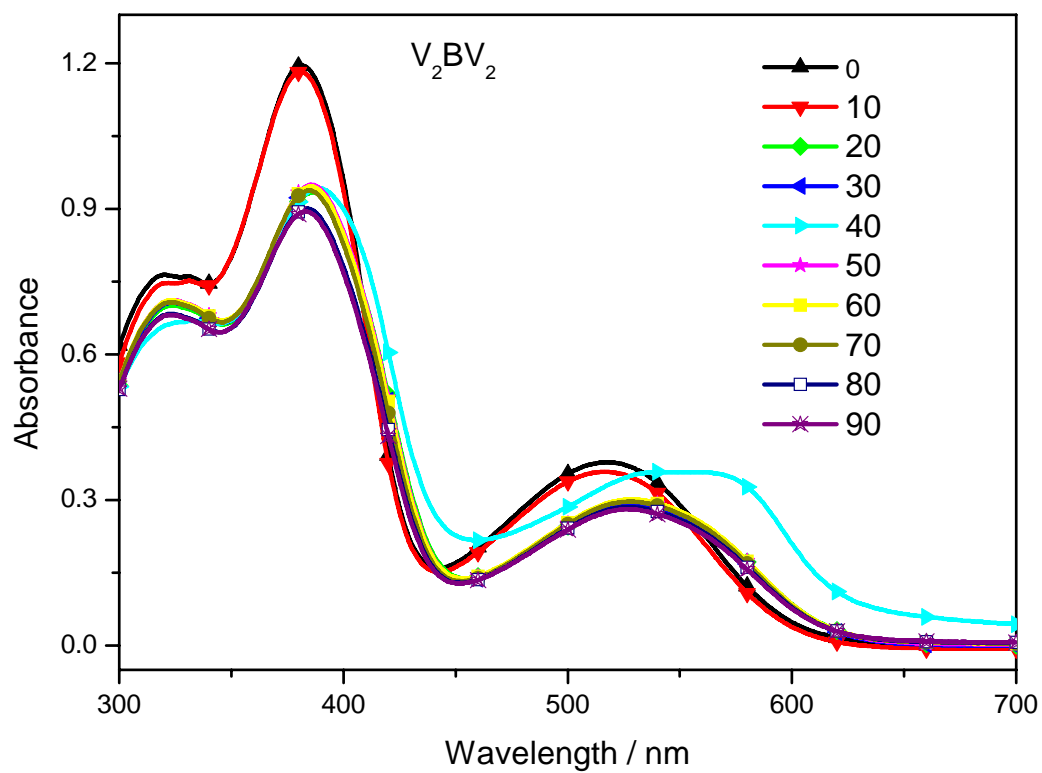


Fig. S3. UV absorption spectra of V_2BV_2 and T_2BT_2 in water/DMF mixtures with different volume fractions of water.

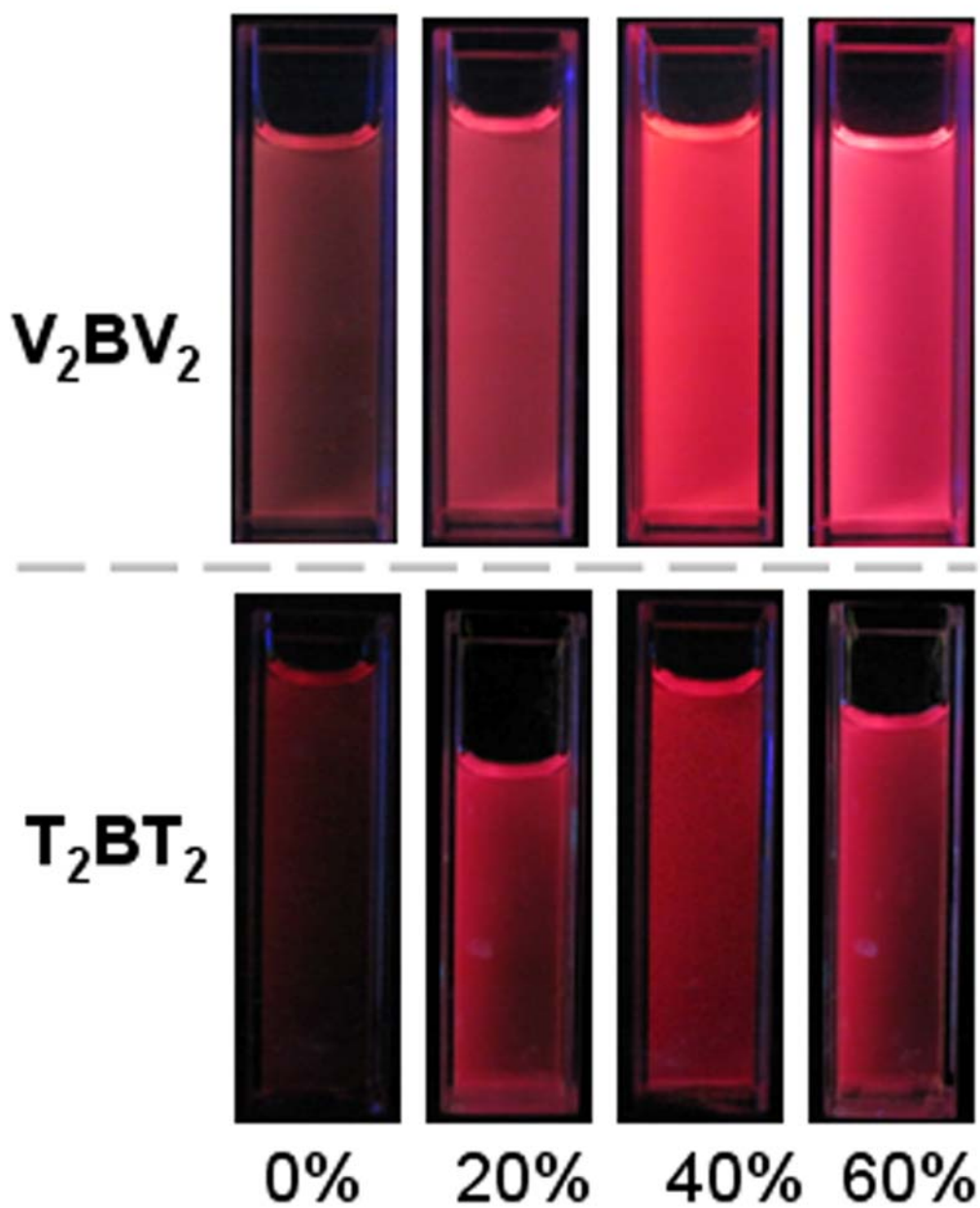


Fig. S4. The emission images of V_2BV_2 and T_2BT_2 in pure DMF, 20%, 40% and 60% water fraction mixtures under 365 nm UV illumination ($5 \mu\text{M}$).

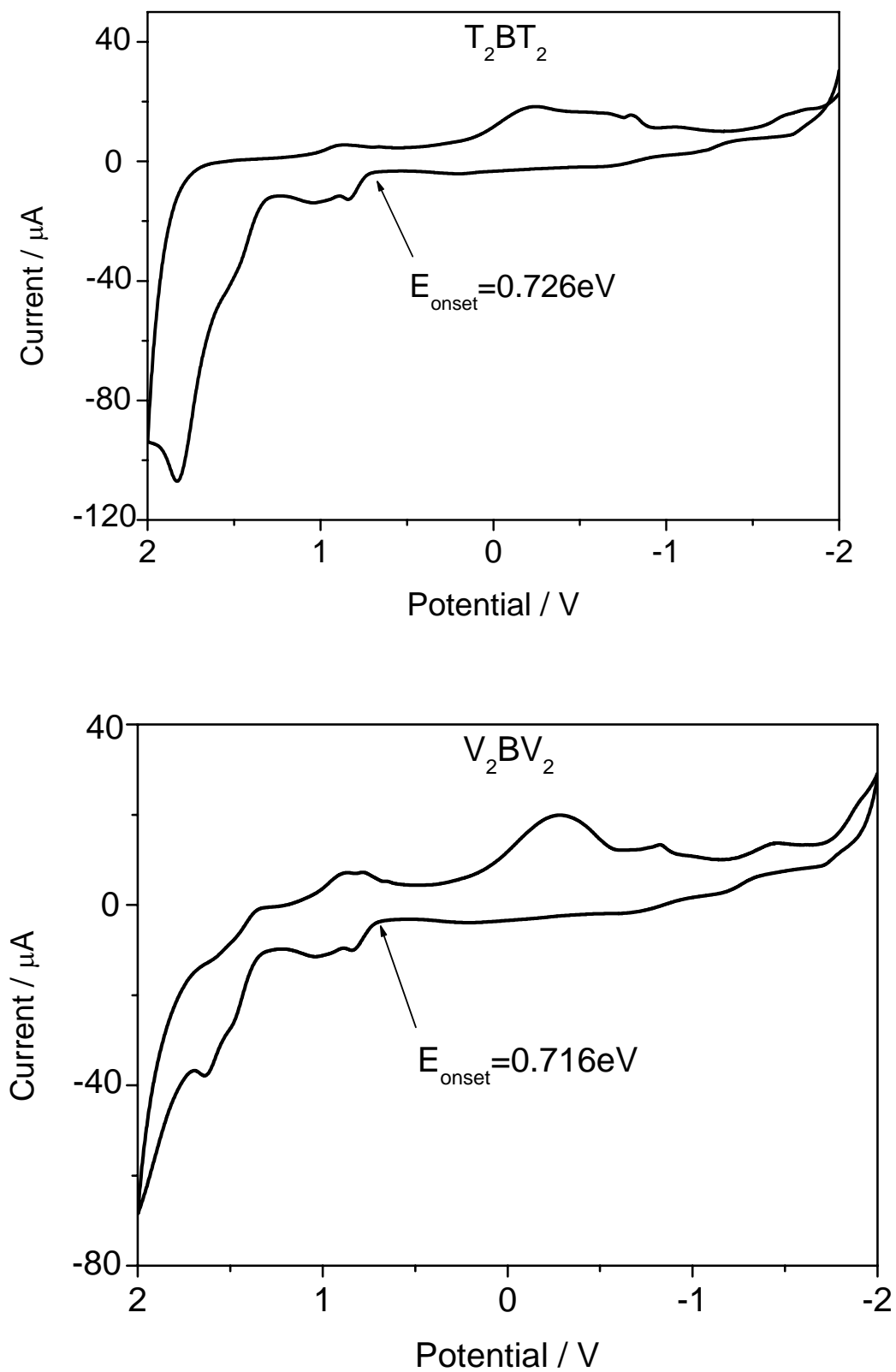


Fig. S5. CV curves of T_2BT_2 and V_2BV_2 in MC.

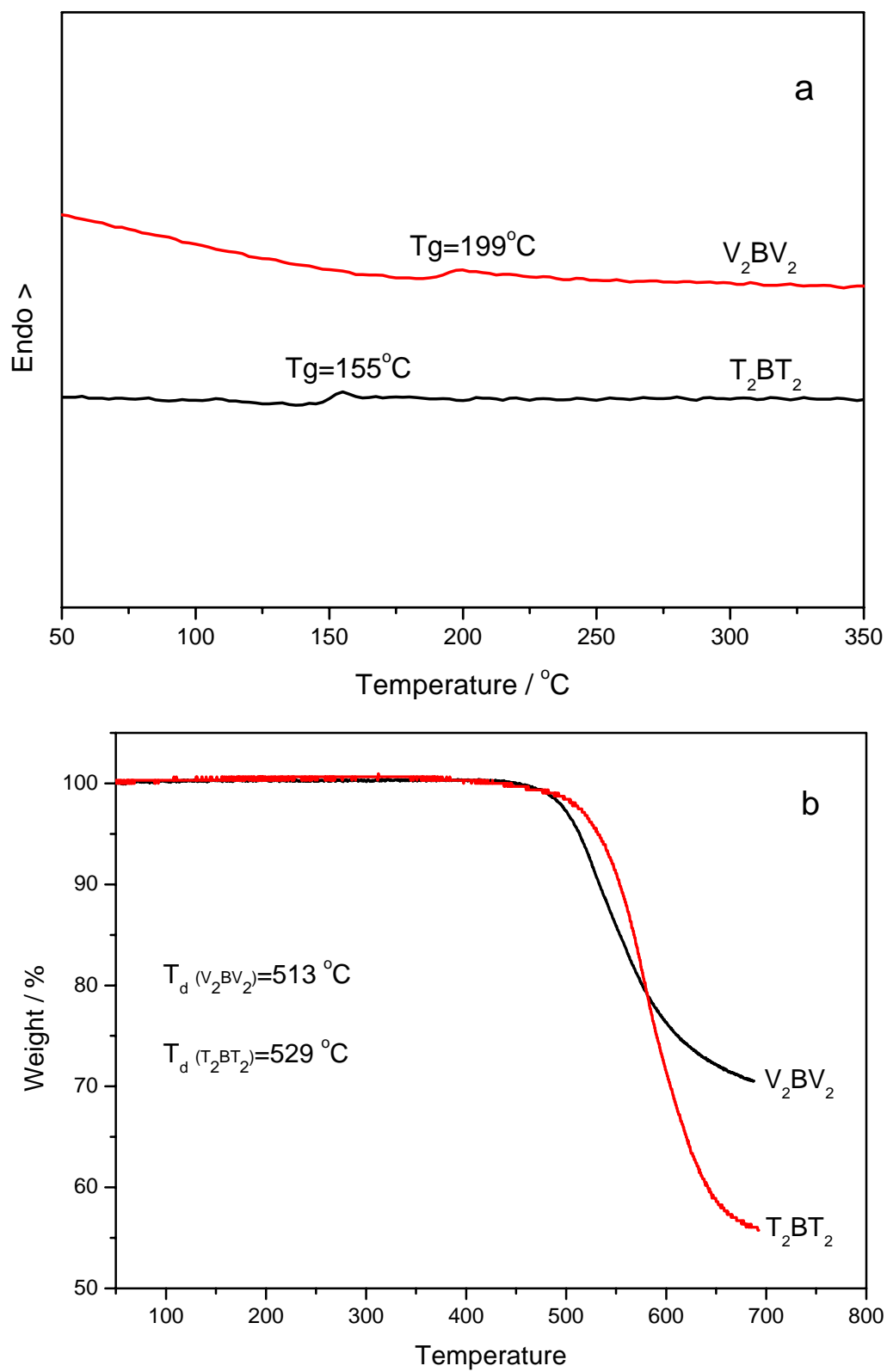


Fig. S6. DSC (a) and TGA (b) curves of V_2BV_2 and T_2BT_2 .

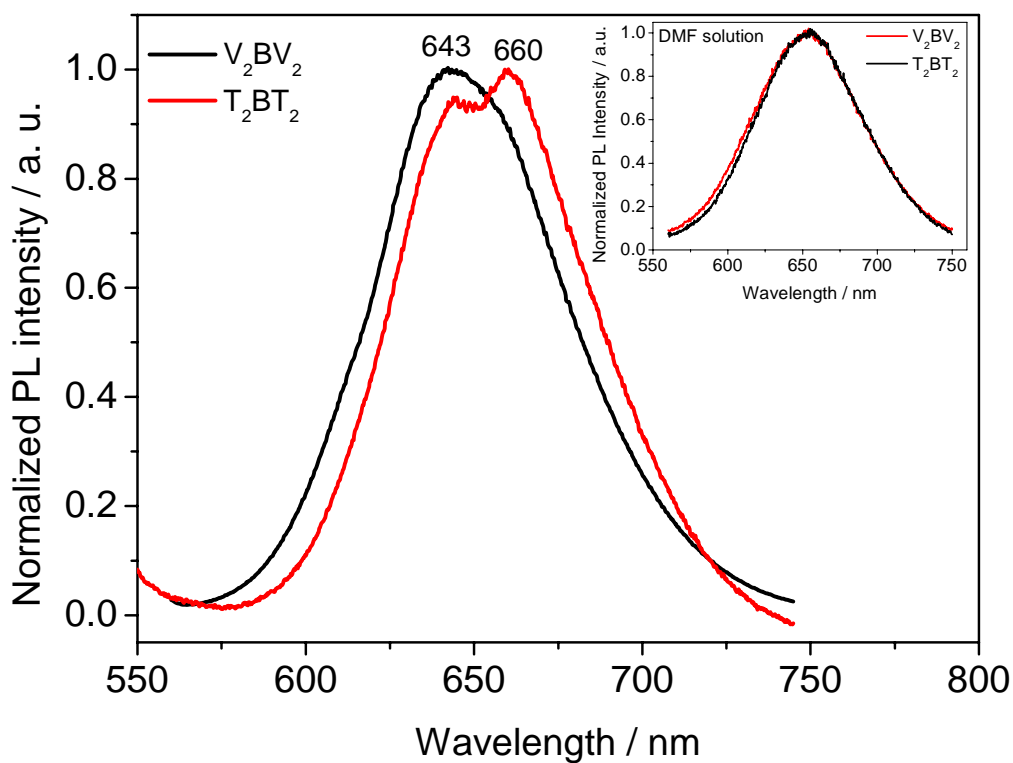
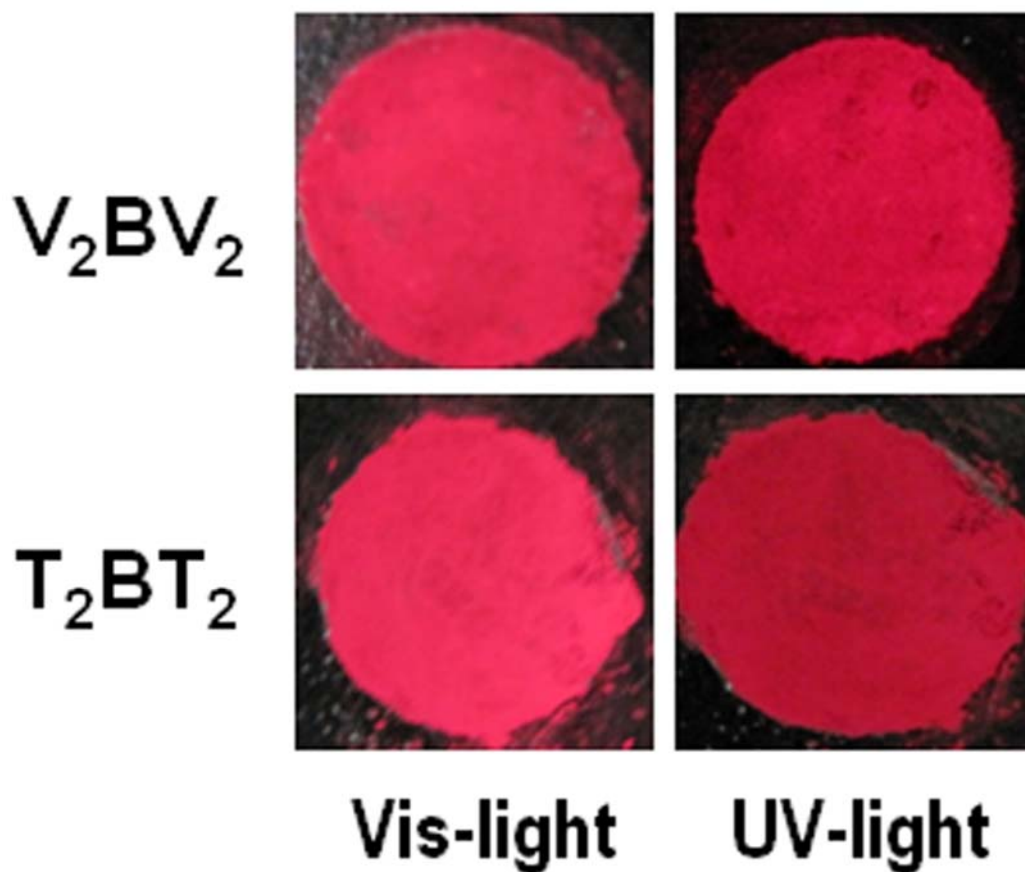


Fig. S7. The powder colors (left) and solid PL spectra (right) of V_2BV_2 and T_2BT_2 (inset, PL spectra of V_2BV_2 and T_2BT_2 in DMF solution).

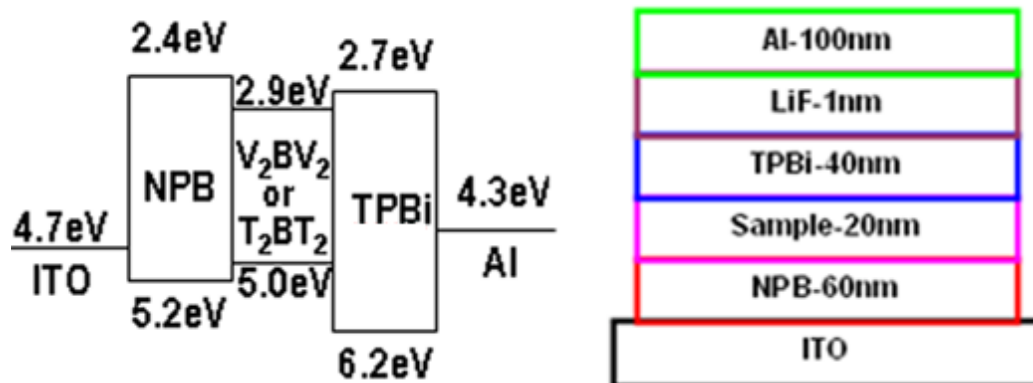


Fig. S8. The energy level diagram and structure of the OLED device.

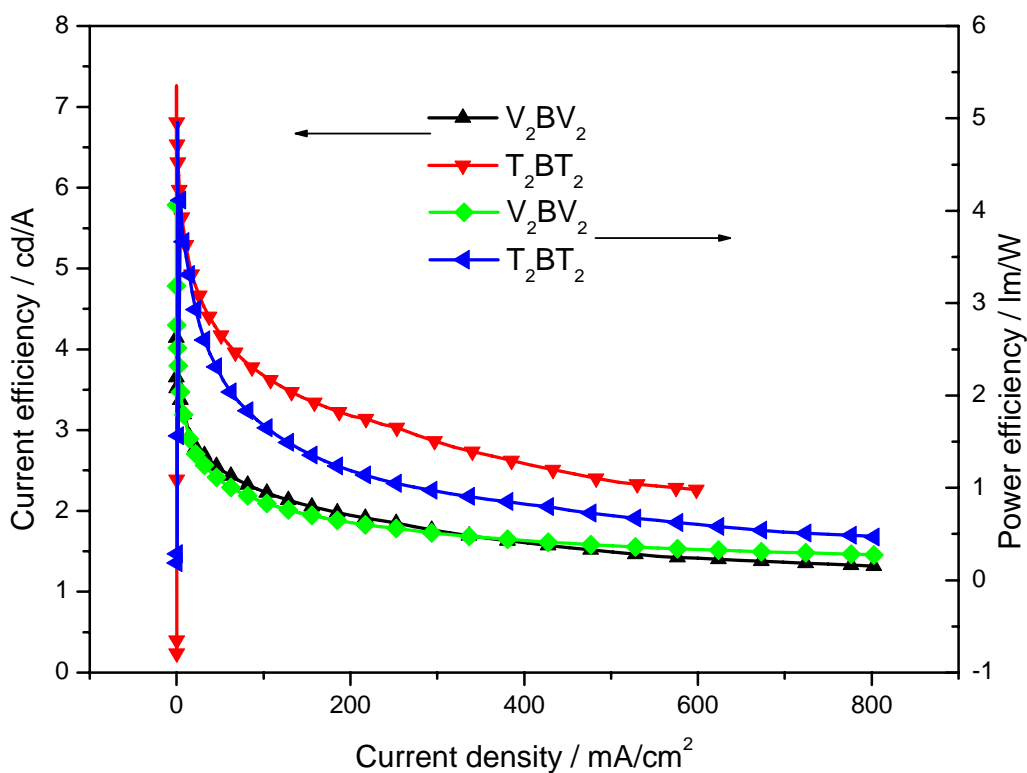


Fig. S9. Current efficiency, and power efficiency vs current density.

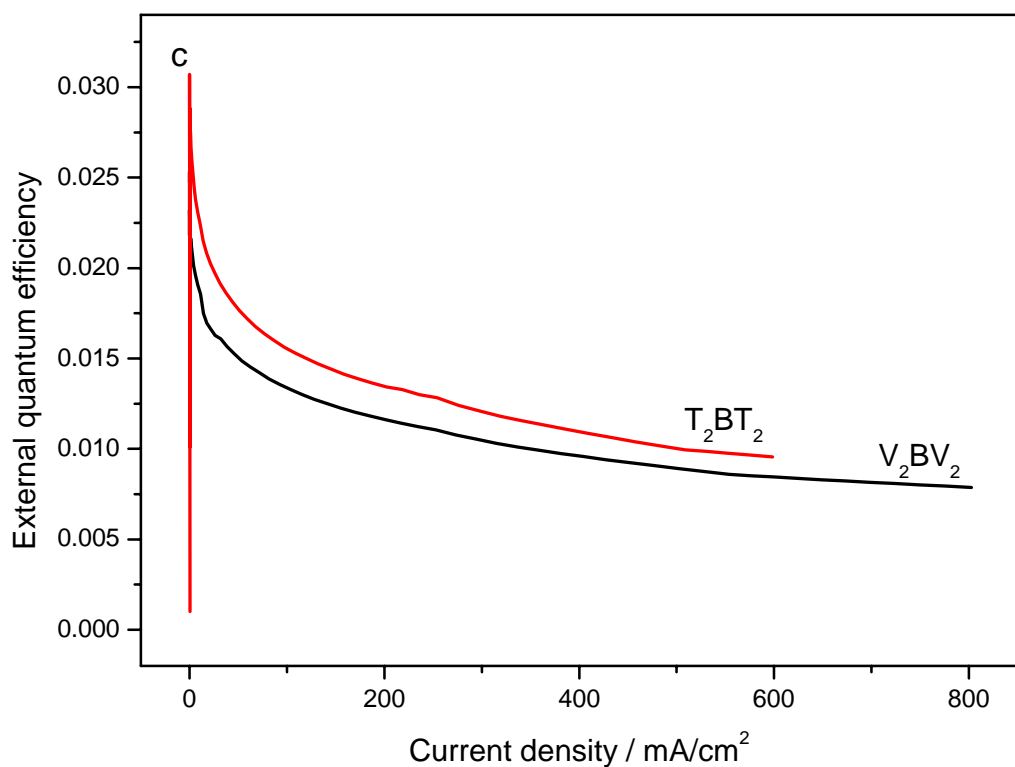


Fig. S10. The device external quantum efficiency vs current density.

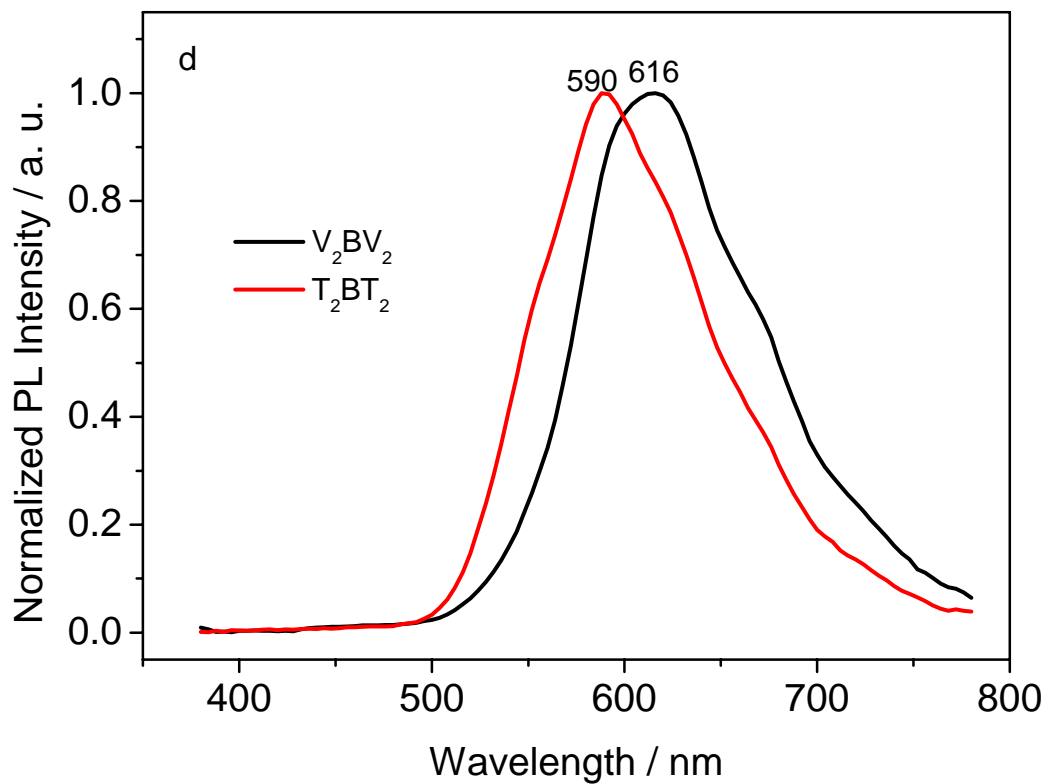


Fig. S11. Electroluminescence spectra of the devices.

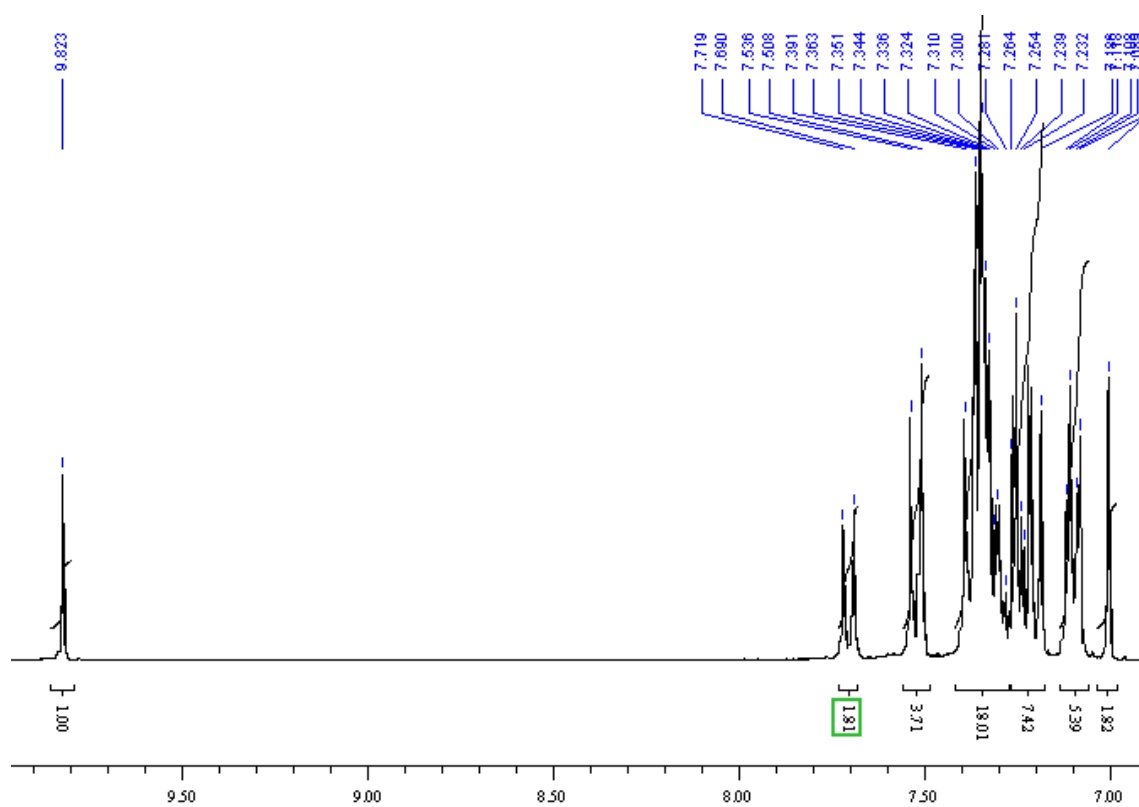


Fig. S12. ^1H -NMR spectrum of $\text{V}_2\text{TPA-CHO}$.

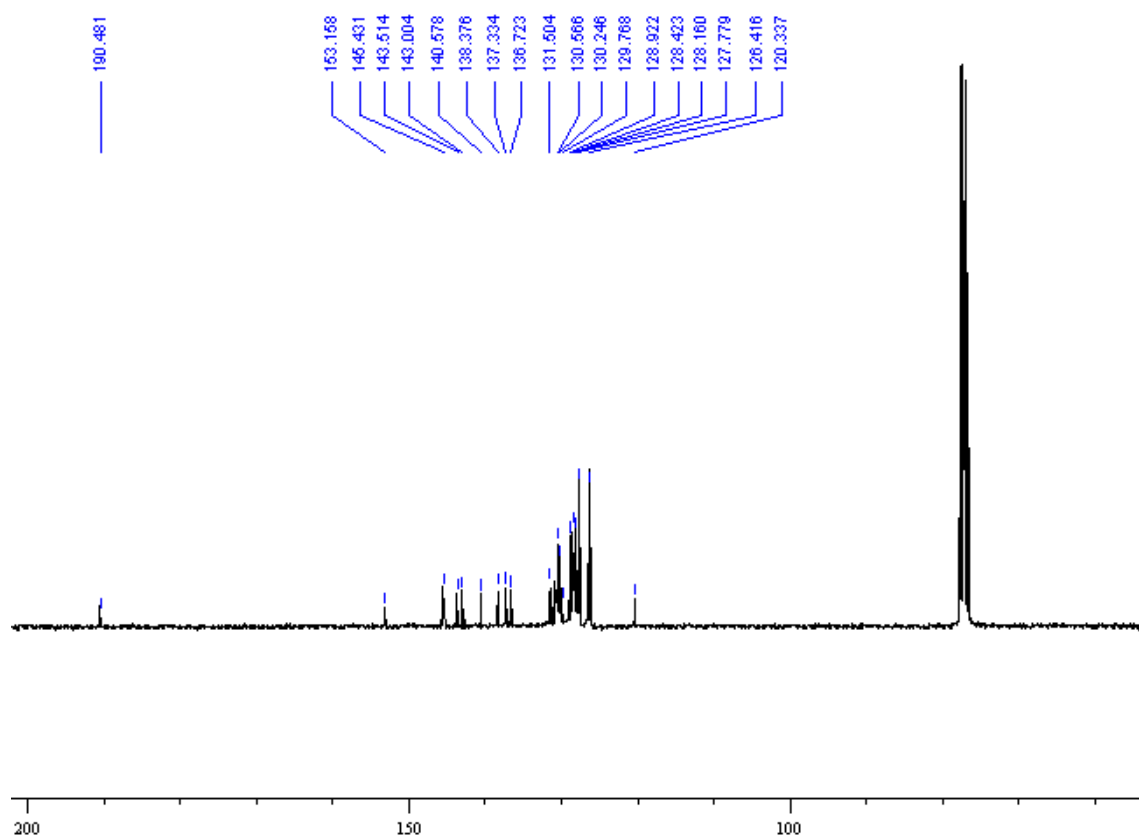


Fig. S13. ^{13}C -NMR spectrum of $\text{V}_2\text{TPA-CHO}$.

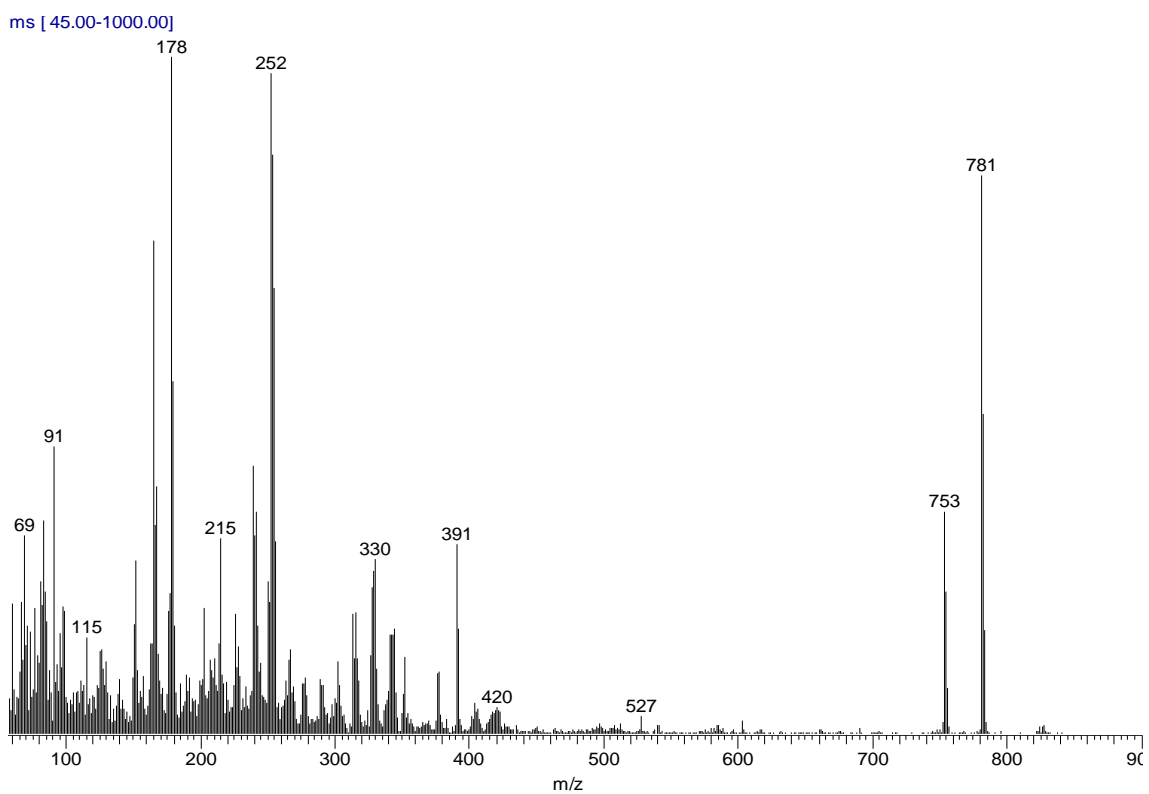


Fig. S14. MS spectrum of V₂TPA-CHO.

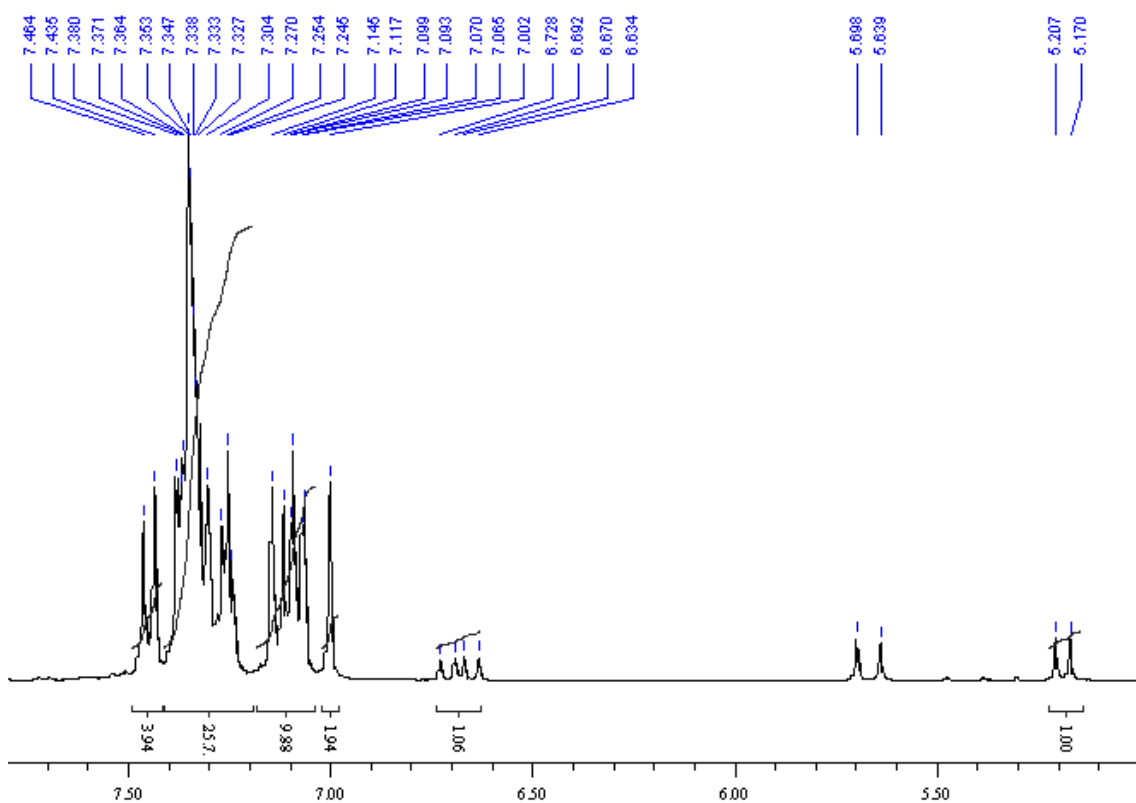


Fig. S15. ¹H-NMR spectrum of V₂TPA-V.

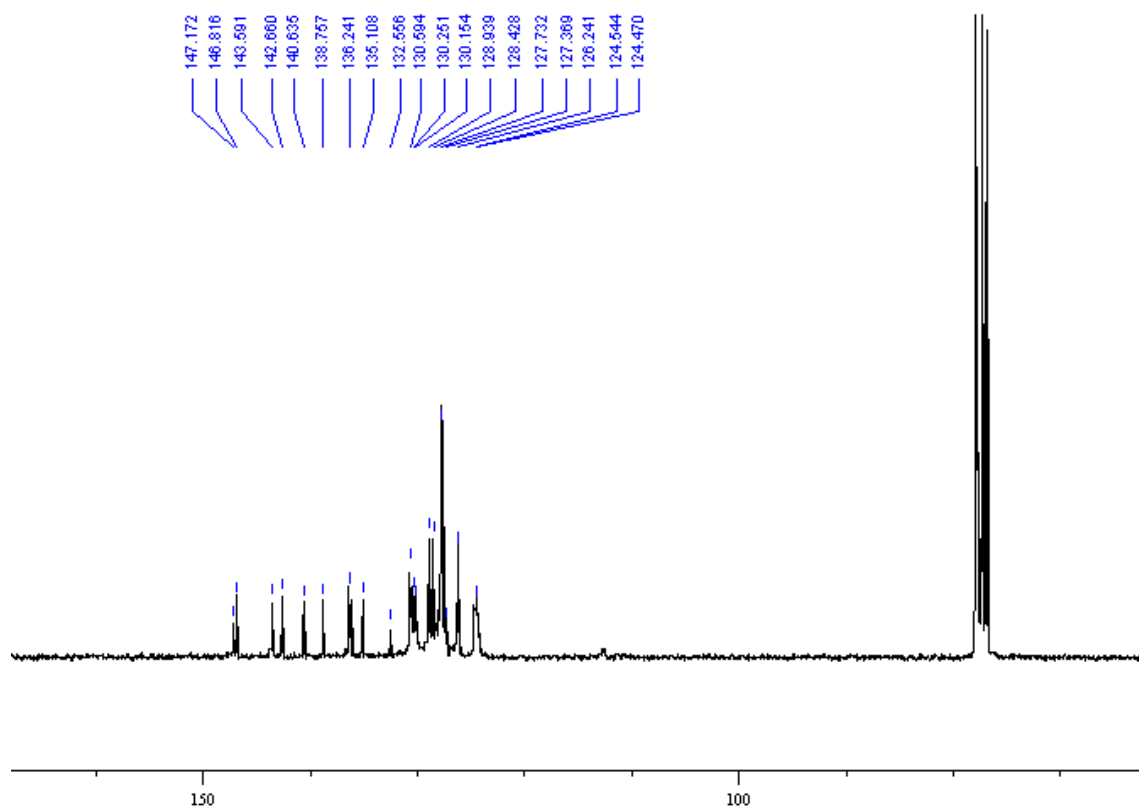


Fig. S16. ^{13}C -NMR spectrum of $\text{V}_2\text{TPA-V}$.

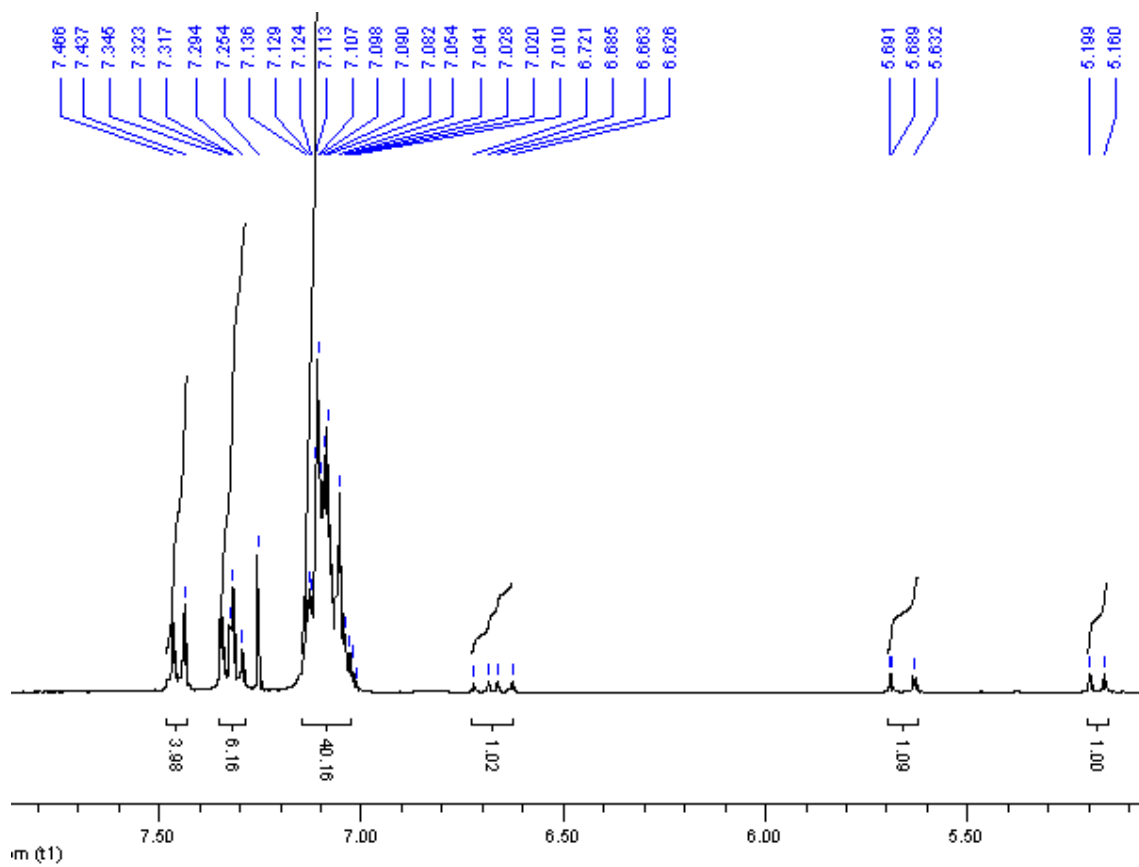


Fig. S17. ^1H -NMR spectrum of $\text{T}_2\text{TPA-V}$.

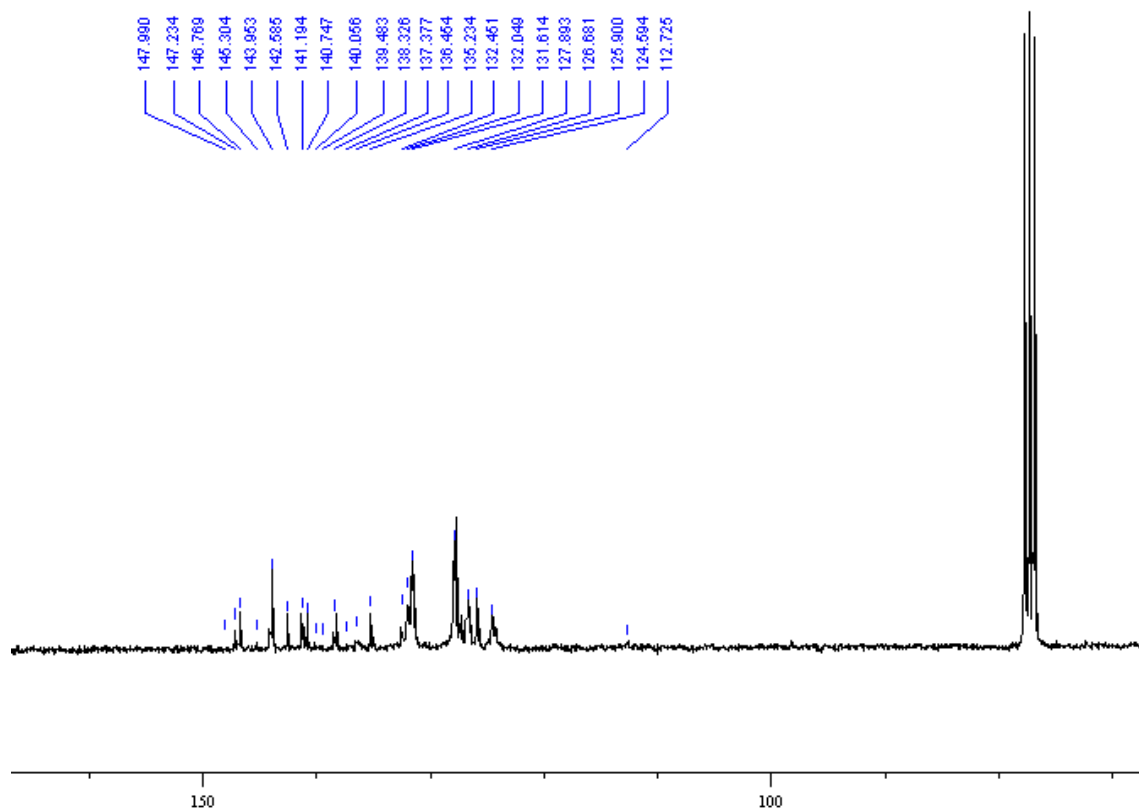


Fig. S18. ^{13}C -NMR spectrum of $\text{T}_2\text{TPA-V}$.

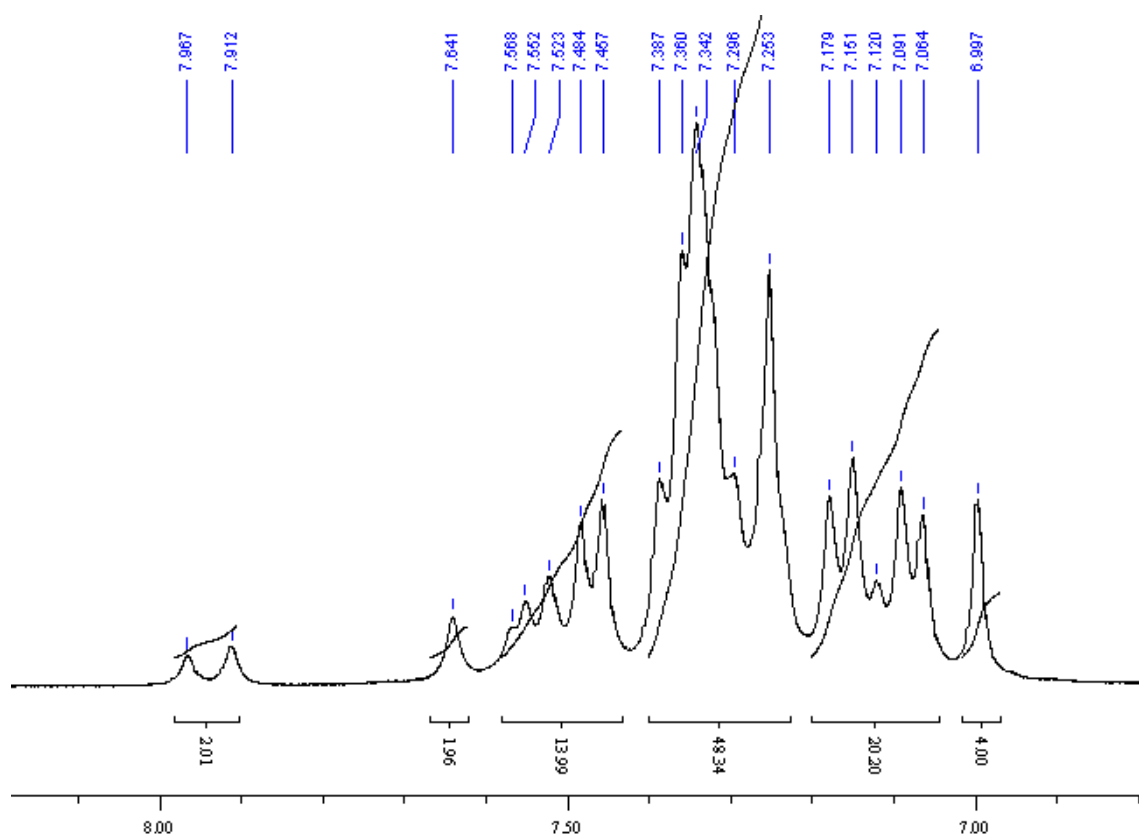


Fig. S19. ^1H -NMR spectrum of V_2BV_2 .

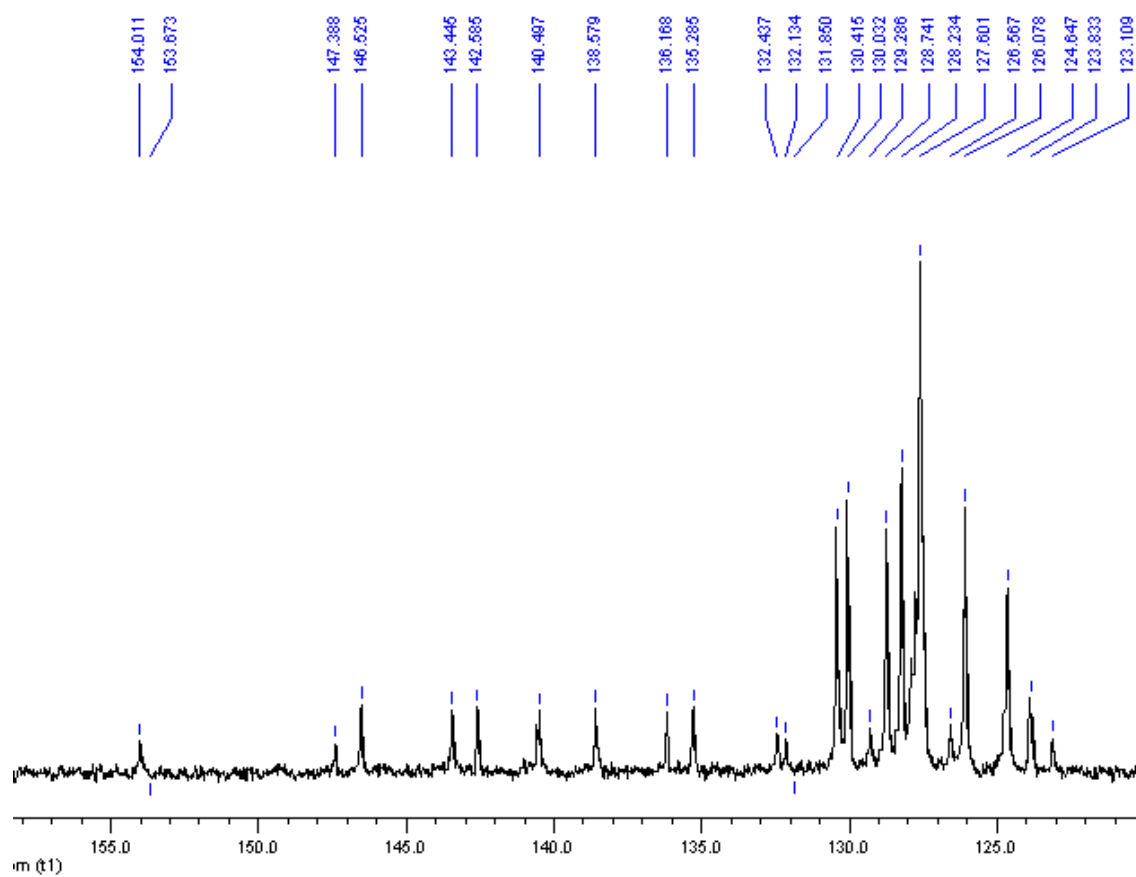


Fig. S20. ^{13}C -NMR spectrum of V_2BV_2 .

Instrument: MAT 95XP (Thermo)

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V2BV2

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T: + c FAB Full ms [99.50-1800.50]

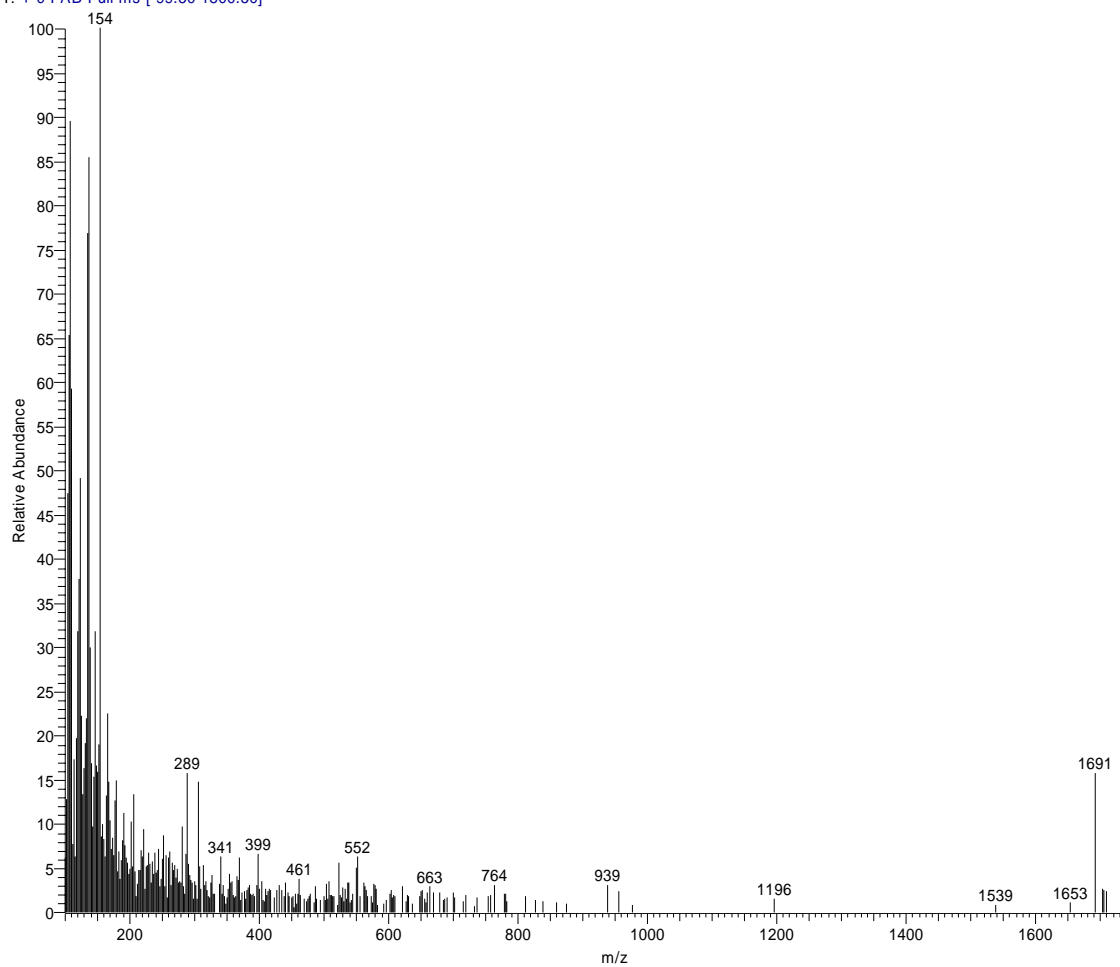


Fig. S21. MS spectrum of V_2BV_2 .

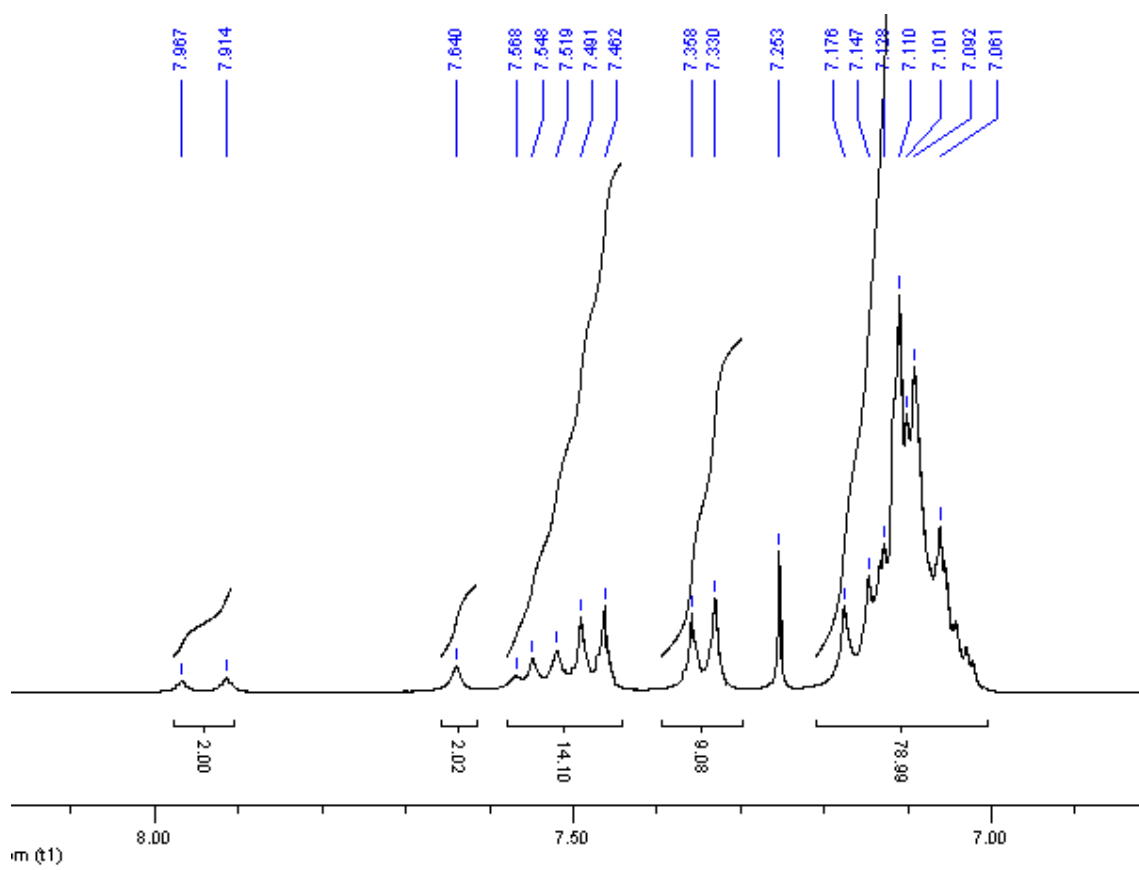


Fig. S22. ¹H-NMR spectrum of T₂BT₂.

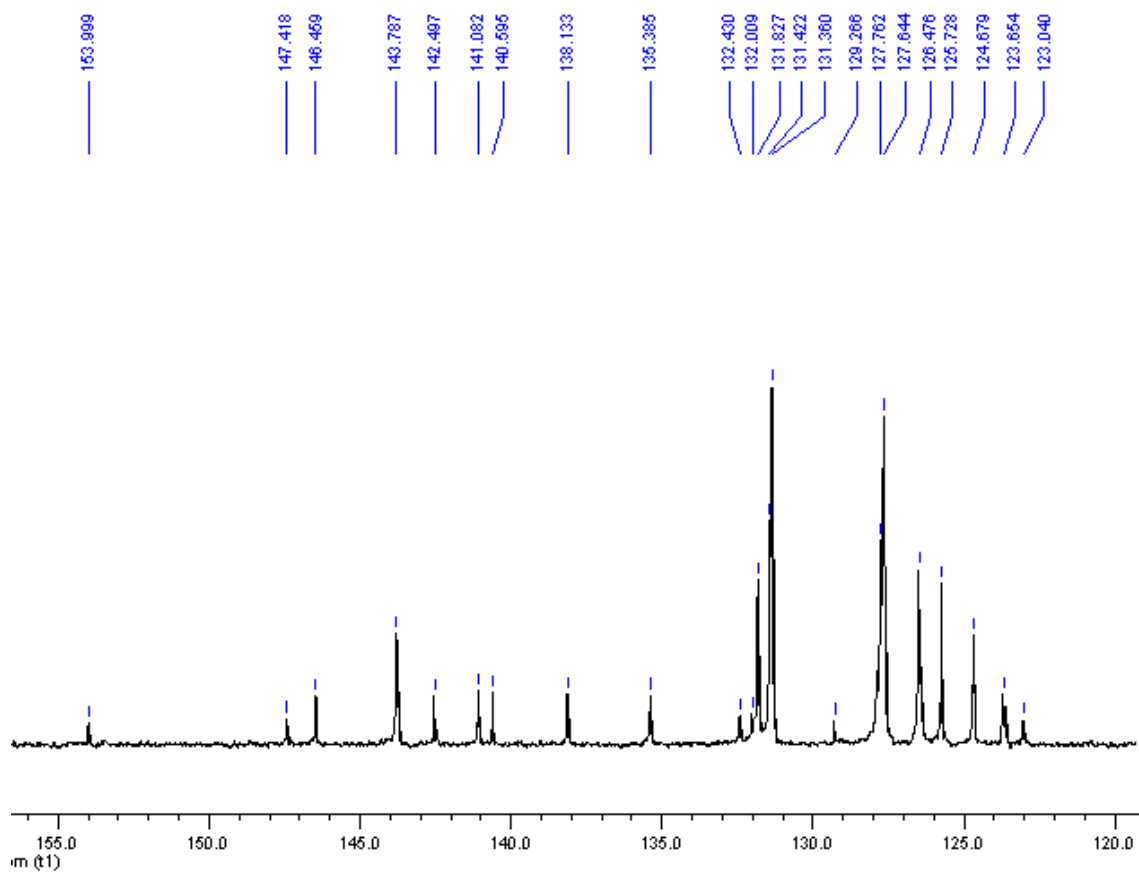


Fig. S23. ¹³C-NMR spectrum of T₂BT₂.

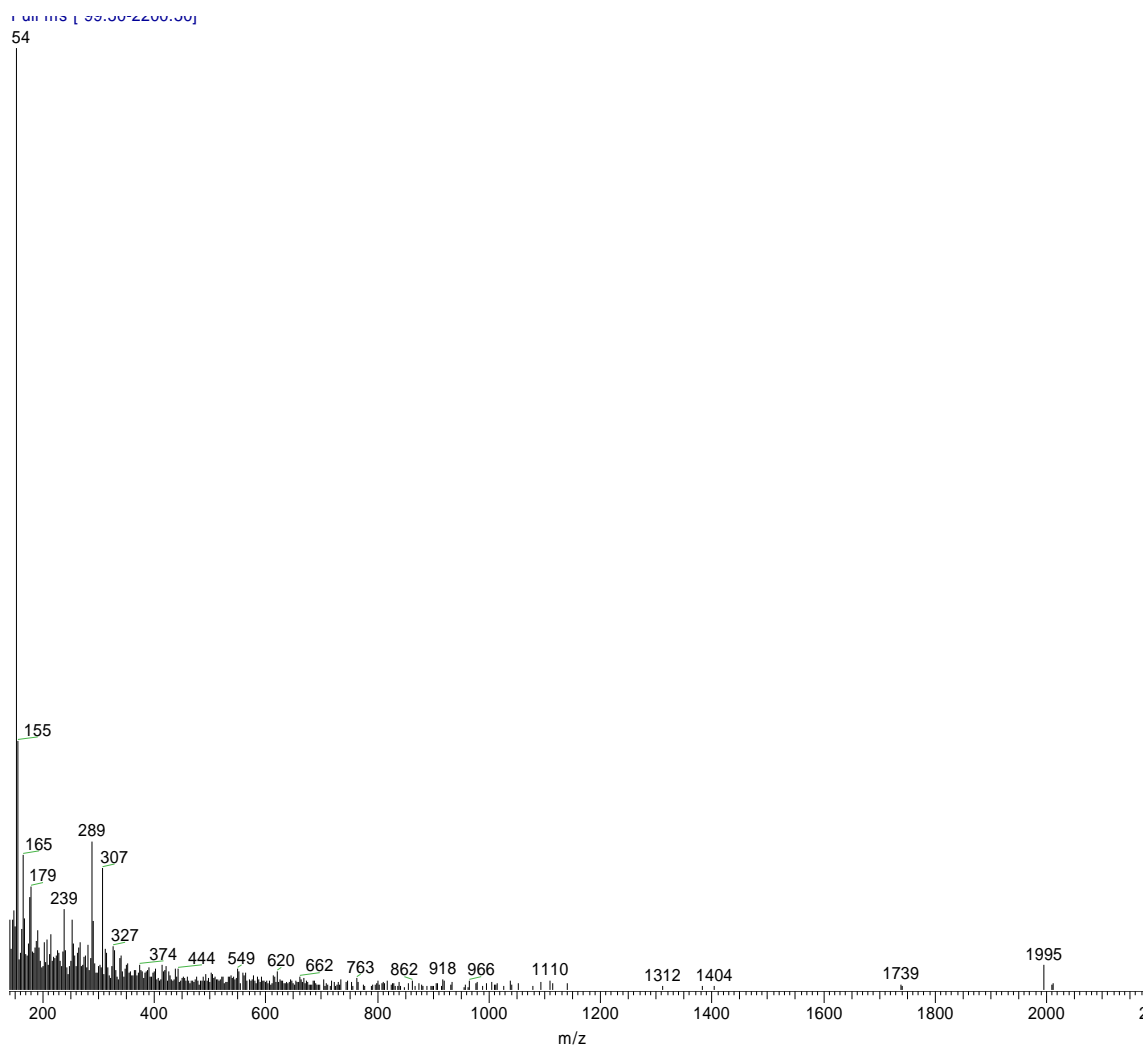


Fig. S24. MS spectrum of T₂BT₂.