Electronic Supplementary Information for

Large core-expanded triazatruxene-based discotic liquid crystals: synthesis, characterization and physical properties

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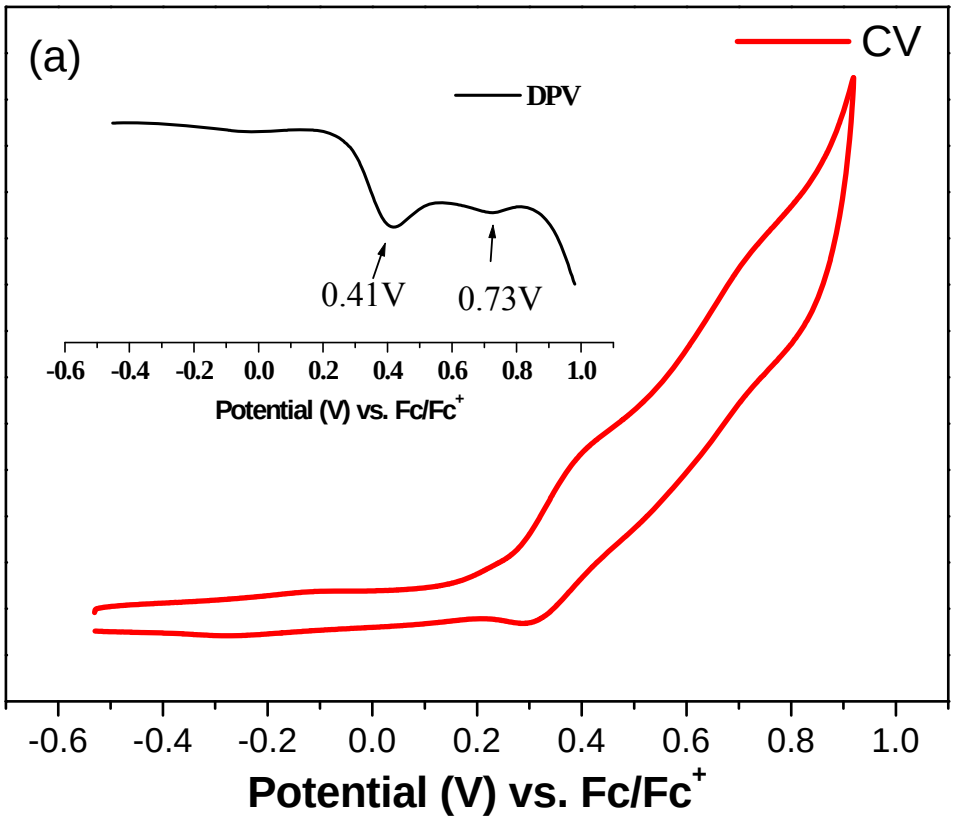
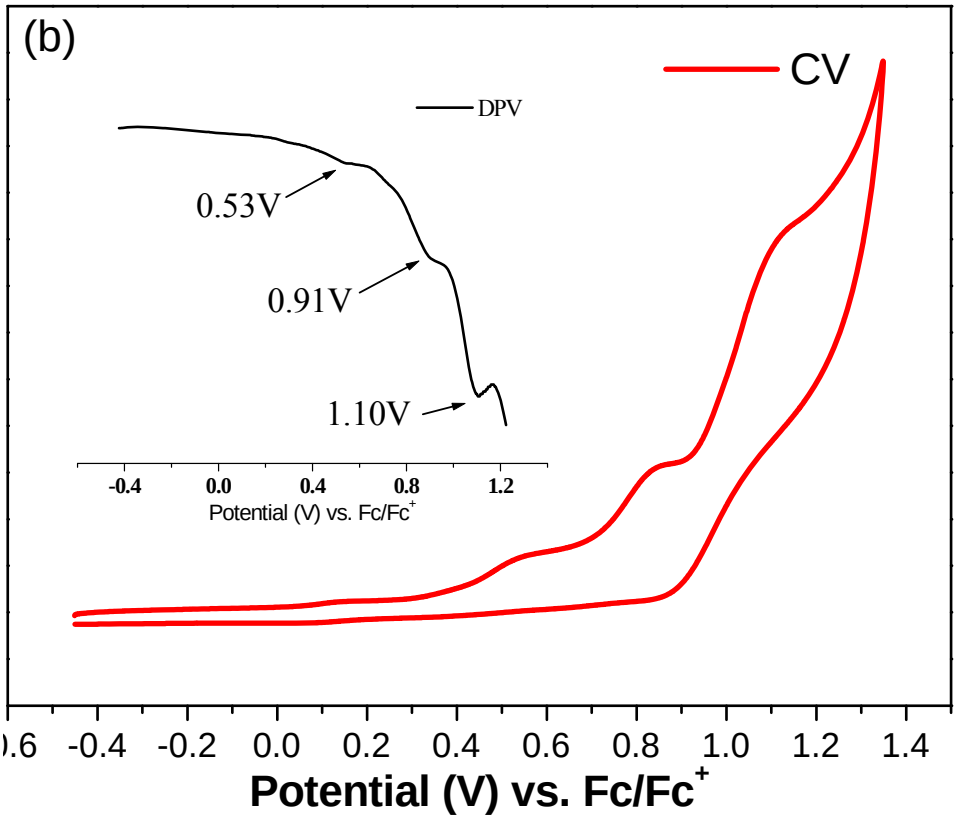
1. General methods

All reagents and starting materials were obtained from commercial sources and used without further purification. Anhydrous toluene and THF were distilled over sodium under nitrogen atmosphere before using. Anhydrous ethanol was distilled over Mg/I_2 under nitrogen. Anhydrous dichloromethane was distilled over CaH_2. Hexa-bromo triazatruxene was prepared according to reported literature.[1] Diketone moieties **DK-1**, **DK-2** and **DK-3** were prepared according to reported literatures.[2] ^{1}H and ^{13}C NMR spectra were recorded using Advance 300MHz and 500MHz Bruker spectrometer in $CDCl_3$. COSY NMR spectroscopy was carried out at Bruker DRX 500 spectrometer. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). MALDI-TOF mass spectra were measured on a Bruker Autoflex MALDI-TOF instrument using 1,8,9-trihydroxyanthracene as the matrix. Elemental analyses (C, H, N) were performed on a Vario EL Elementar (Elementar Analyzen-systeme, Hanau, Germany). UV-vis absorption and fluorescence spectra were recorded on a Shimadzu UV-1700 spectrophotometer and a RF- 5301 fluorometer, respectively. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed in dry dichloromethane or dry chlorobenzene on a CHI 620C electrochemical analyzer with a three-electrode cell, using 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, gold disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s. The potential was externally calibrated against the ferrocene/ferrocenium couple. Thermogravimetric analysis (TGA) was carried out on a TA instrument 2960 at a heating rate of 10 ºC/min under nitrogen flow. Differential scanning calorimetry (DSC) was performed on a TA instrument 2920 at a heating/cooling rate of 10 ºC/min under nitrogen flow. The initial phase transitions and corresponding temperatures were determined by the OLYMPUS BX51 polarizing optical microscope (POM) equipped with a Linkam TP94 programmable hot stage. Room temperature XRD measurements were performed on a Bruker-AXS D8 DISCOVER with GADDS Powder X-ray diffractometer with Cu Kα radiation.

2. CV and DPV data of TAT-1, 4 and TAT-2





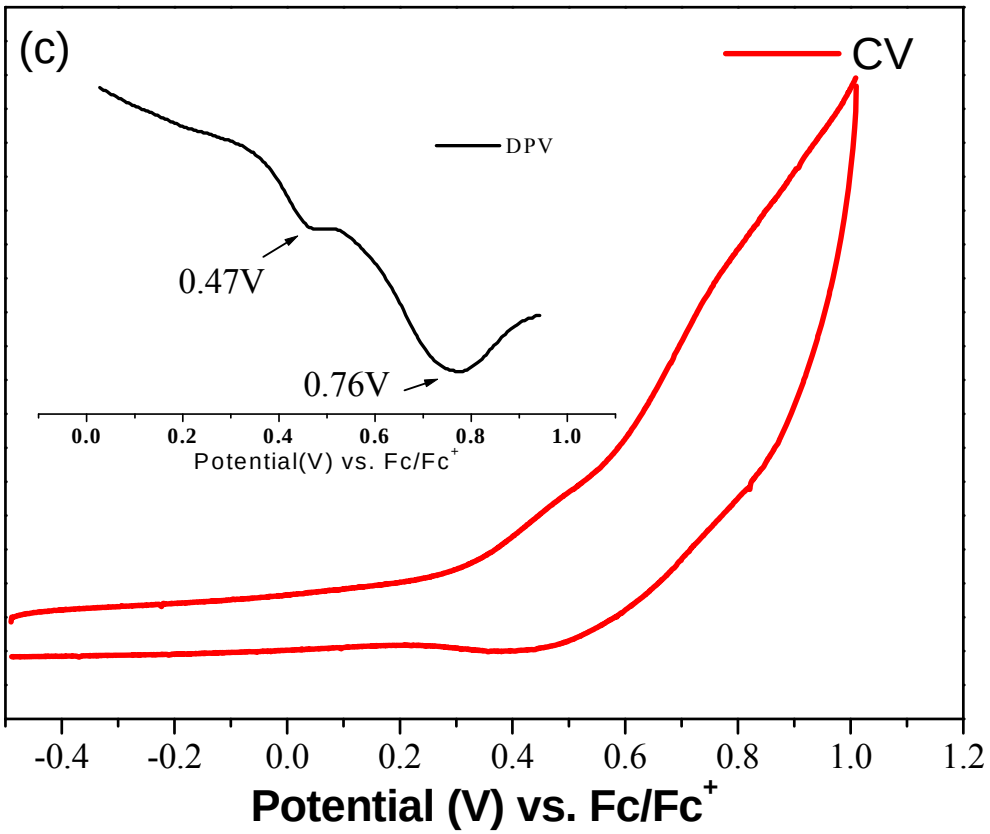


Figure S1. Cyclic voltammograms and differential pulse voltommograms of (a) **TAT-1**, (b) **4** and (c) **TAT-2**.

3. COSY and NOESY NMR spectra of TAT-1

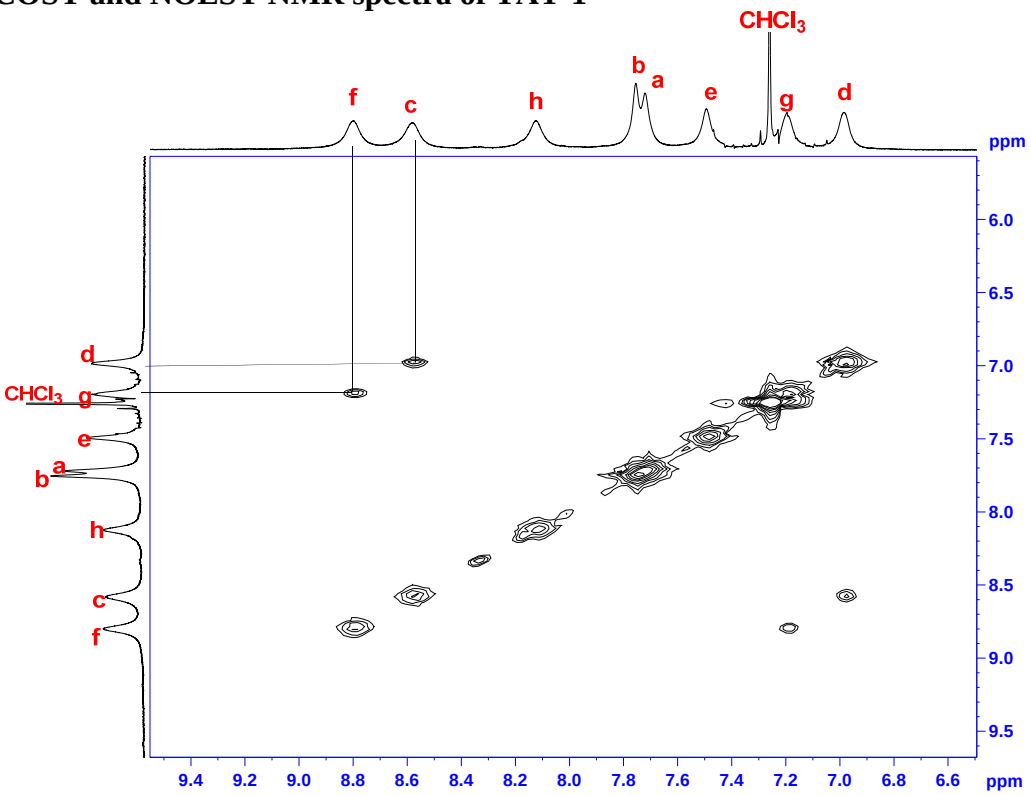


Figure S2 (a). Amplified aromatic region of the COSY spectrum of **TAT-1.** The assignment of the aromatic protons is correlated to the labelled structure shown in Scheme 1 in main text.

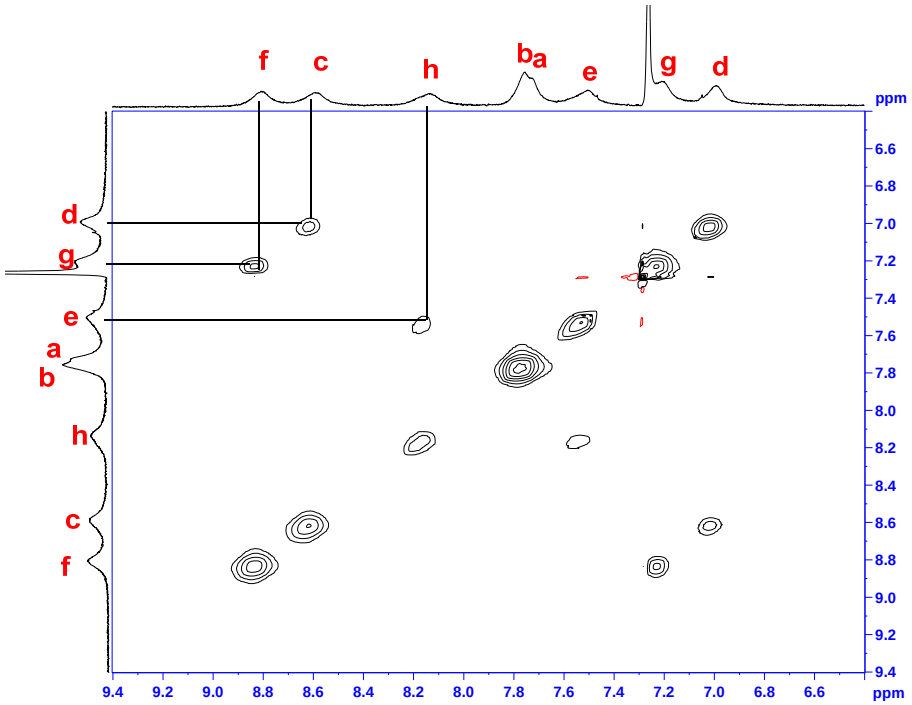


Figure S2 (b). NOESY spectrum of **TAT-1**.

4. Thermal gravity analysis (TGA) of TAT-1 and TAT-2

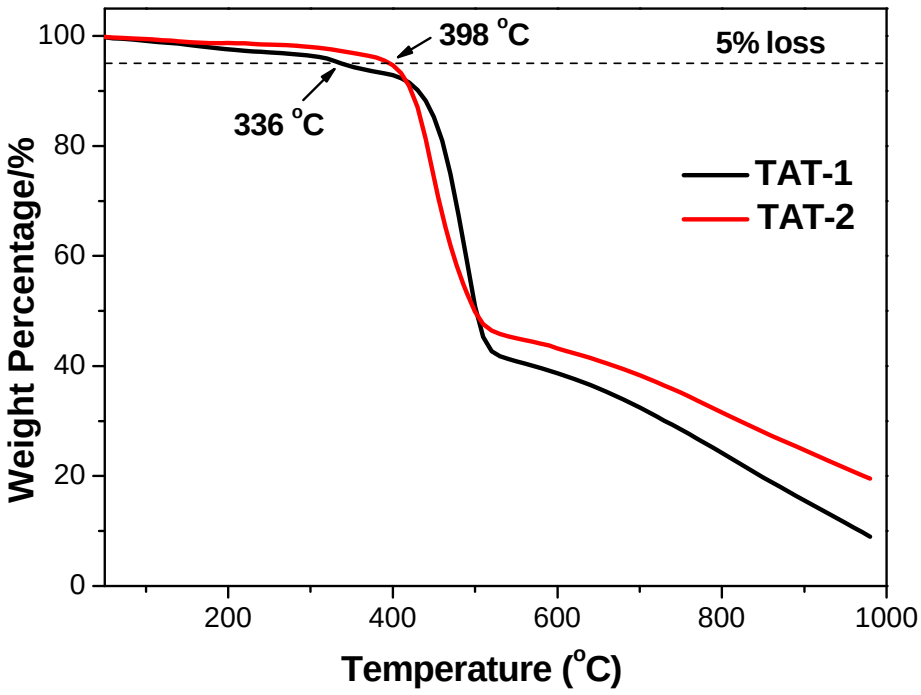


Figure S3. TGA curves for **TAT-1** and **TAT-2** measured under nitrogen with heating rate of 10°C/min.

5. References

(1) (a) García-Frutos, E. M.; Gómez-Lor, B. *J. Am. Chem. Soc.*, **2008**, *130*, 9173. (b) Shao, J.; Guan, Z.; Yan, Y.; Jiao, C.; Xu, Q.; Chi, C. *J. Org. Chem.*, **2011**, *76*, 780.

(2) (a) Foster, E. J.; Babuin, J.; Nguyen, N.; Williams, V. E. *Chem. Commun.*, **2004**, 2052 and references cited therein. (b) Lavigueur, C.; Foster, E. J.; Williams, V. E. *J. Am. Chem. Soc.*, **2008**, *130*, 11791 and references cited therein. (c) Mondal, R.; Ko, S.; Verploegen, E.; Becerril, H. A.; Toney, M.F.; Bao, Z. *J. Mater. Chem.*, **2011**, *21*, 1537.

6. ^{1}H, ^{13}C NMR spectra of TAT-1, 4 and TAT-2.

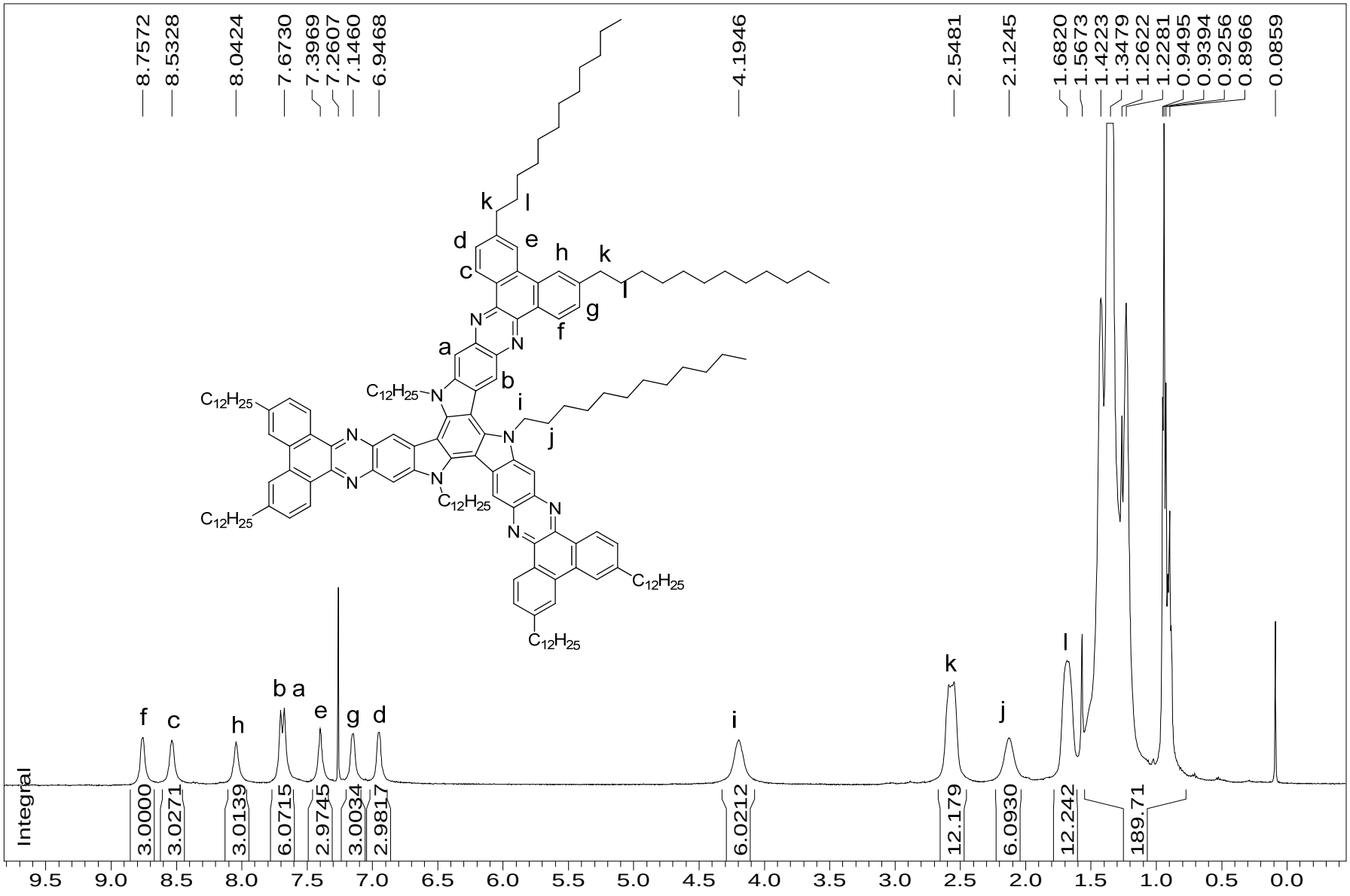


Figure S4. ^{1}H NMR spectrum of **TAT-1** (500 MHz, $CDCl_3$, room temperature).

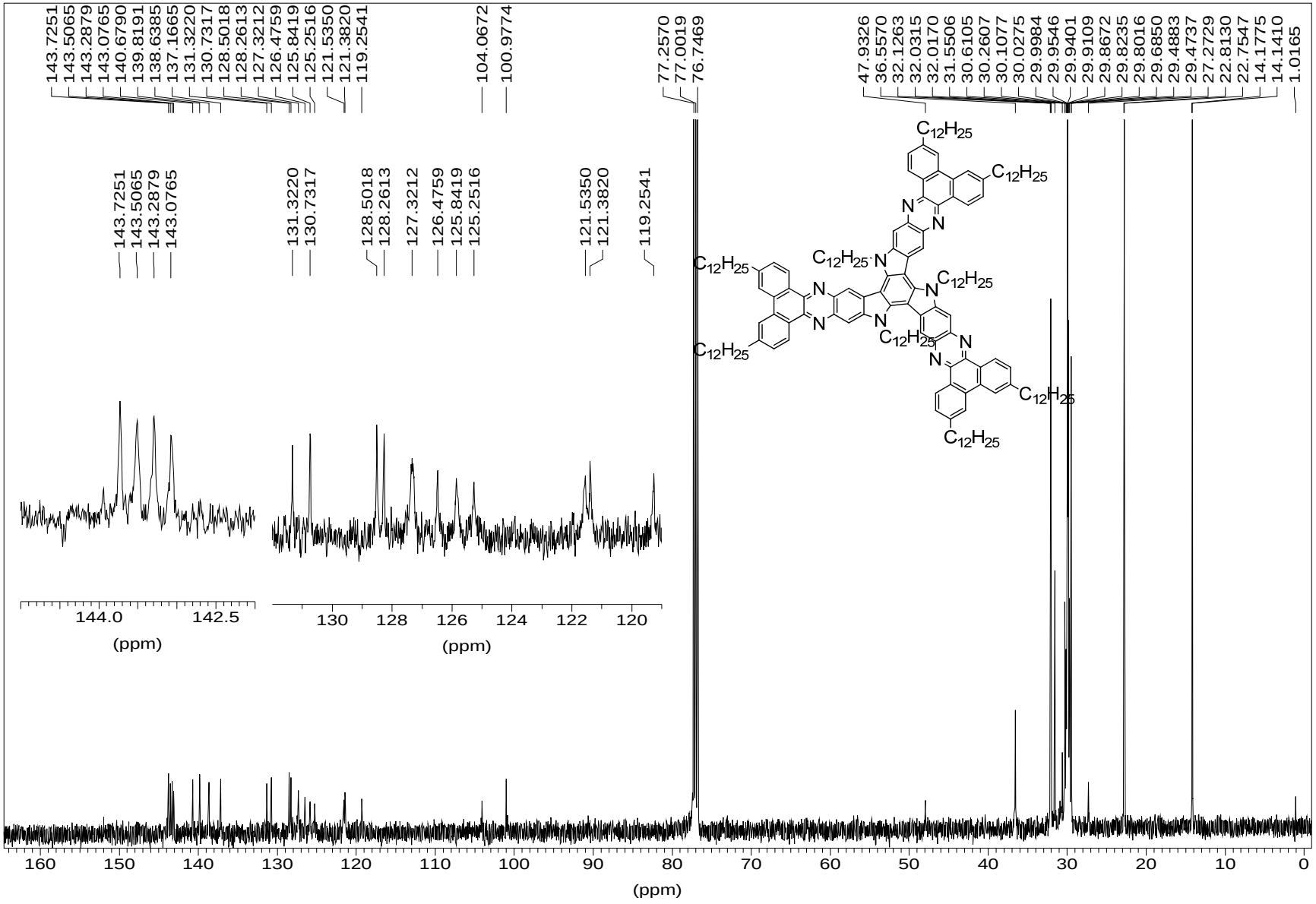


Figure S5. ^{13}C NMR spectrum of **TAT-1** (125 MHz, $CDCl_3$, room temperature).

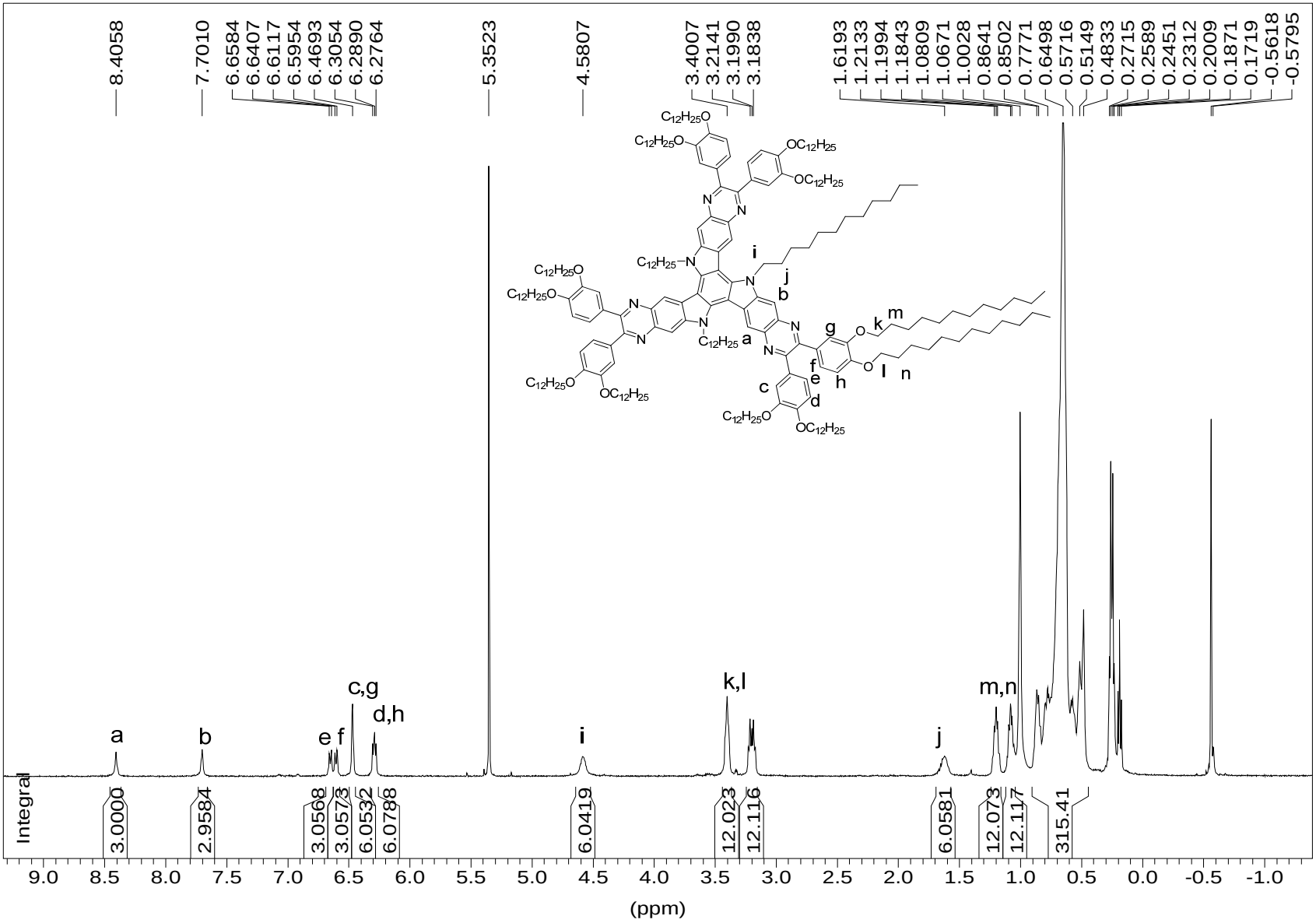


Figure S6. ^{1}H NMR spectrum of compound **4** (500 MHz, CD_2Cl_4, room temperature).

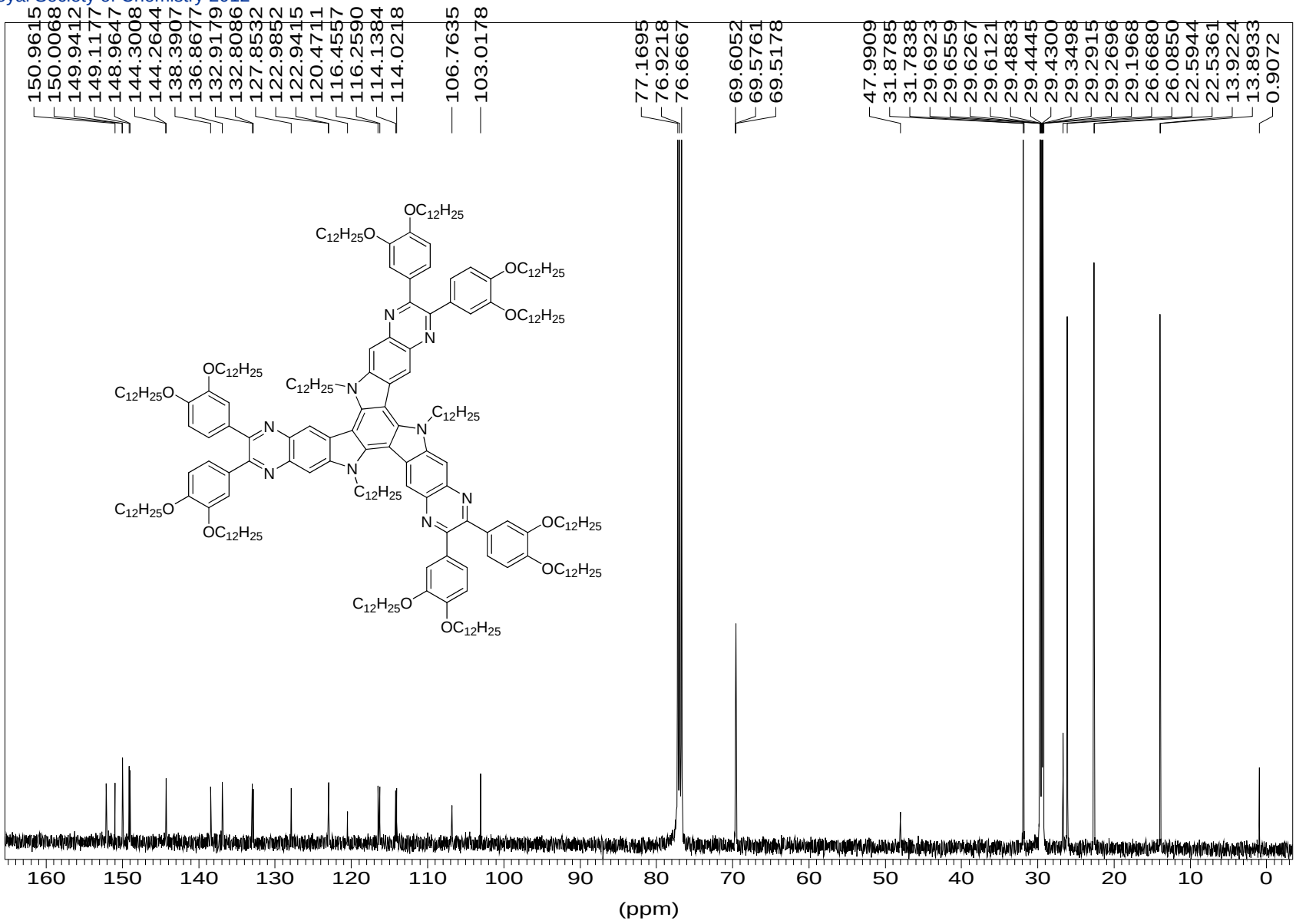


Figure S7. ^{13}C NMR spectrum of compound **4** (125 MHz, $CDCl_3$, room temperature).

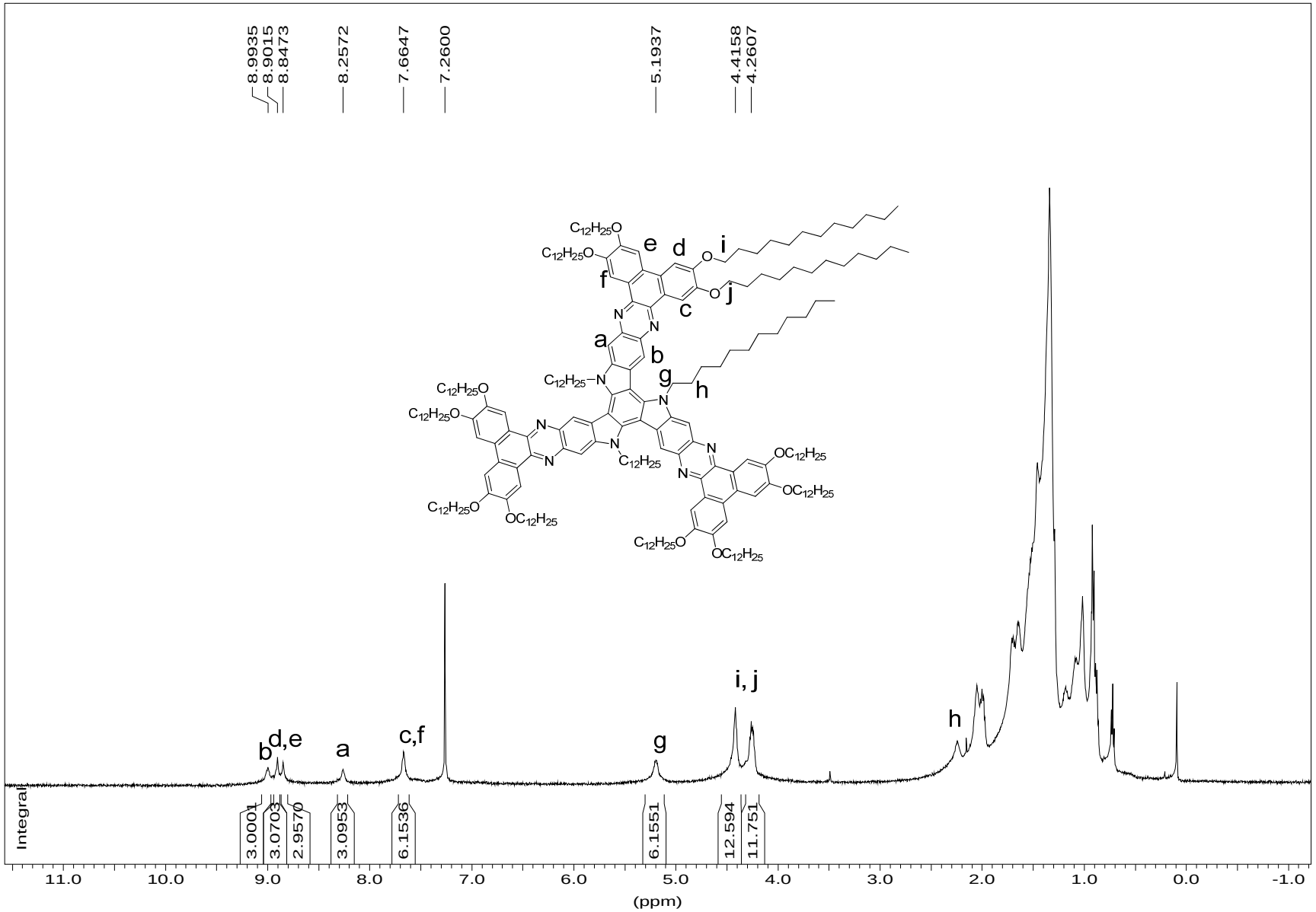


Figure S8. ^{1}H NMR spectrum of **TAT-2** (500 MHz, $CDCl_3$, 50 ^{o}C).

7. MALDI-TOF MS spectra of 4, TAT-1, and TAT-2

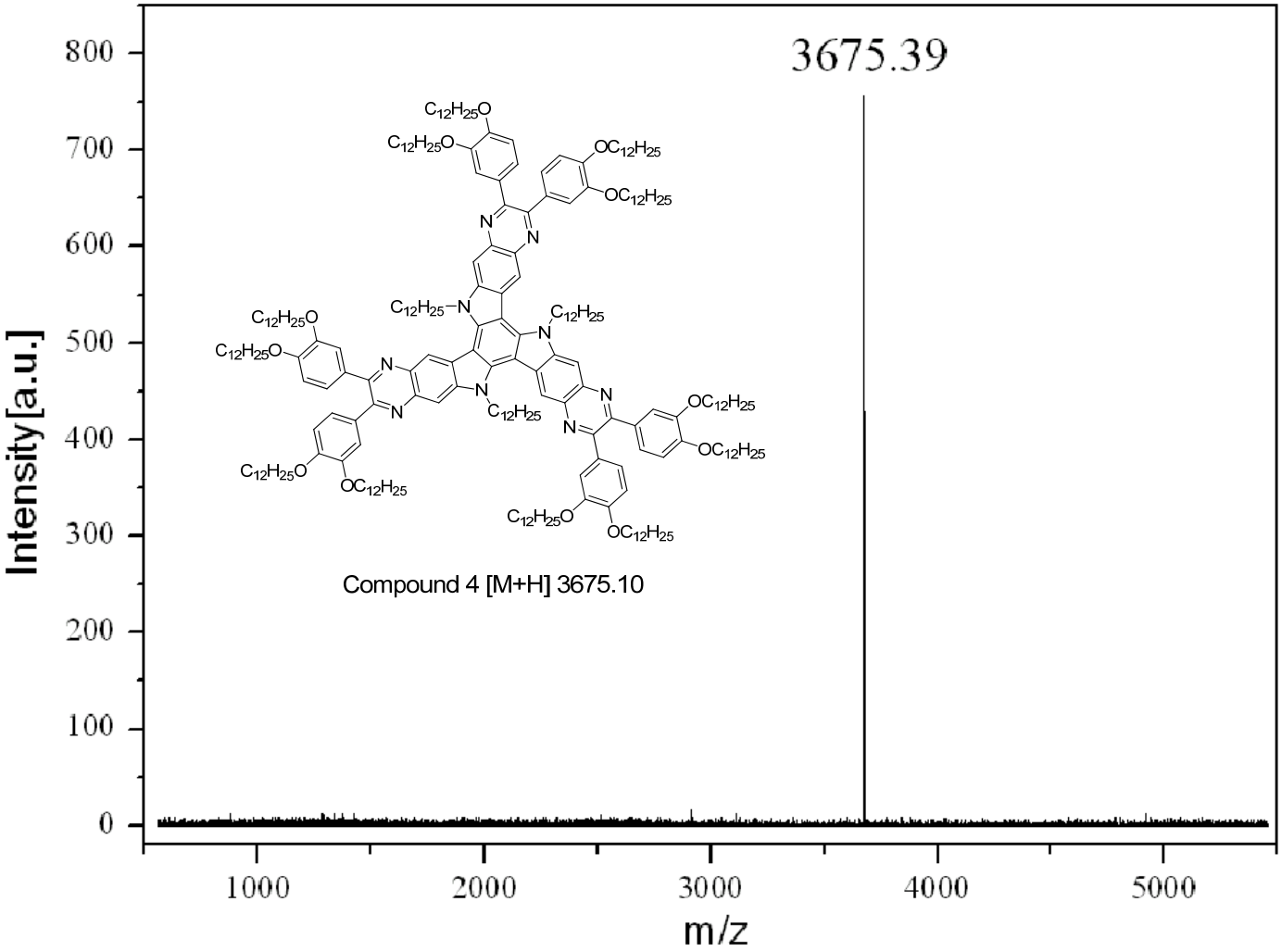


Figure S9: MALDI-TOF MS spectrum of Compound **4**

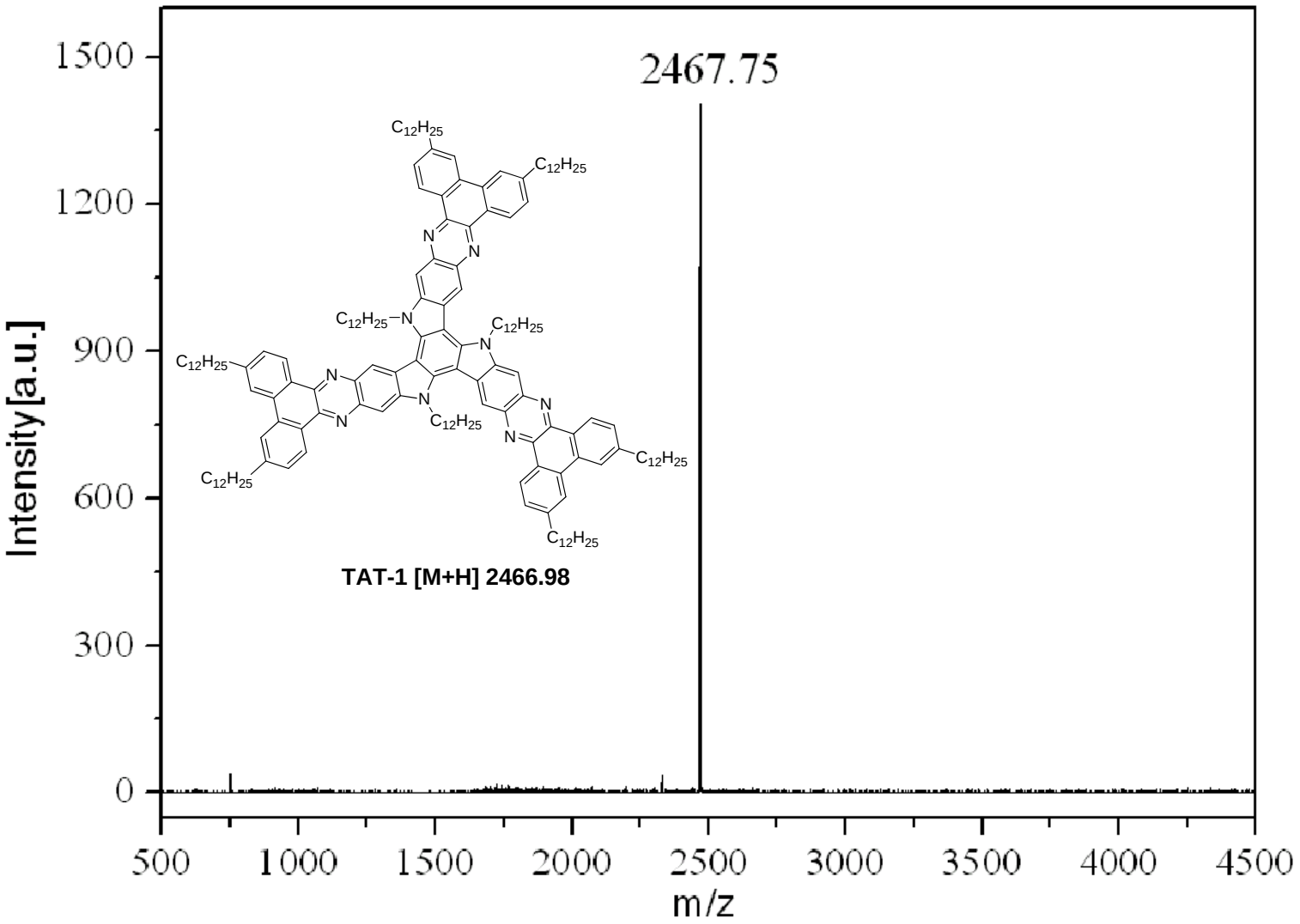


Figure S10: MALDI-TOF MS spectrum of **TAT-1**

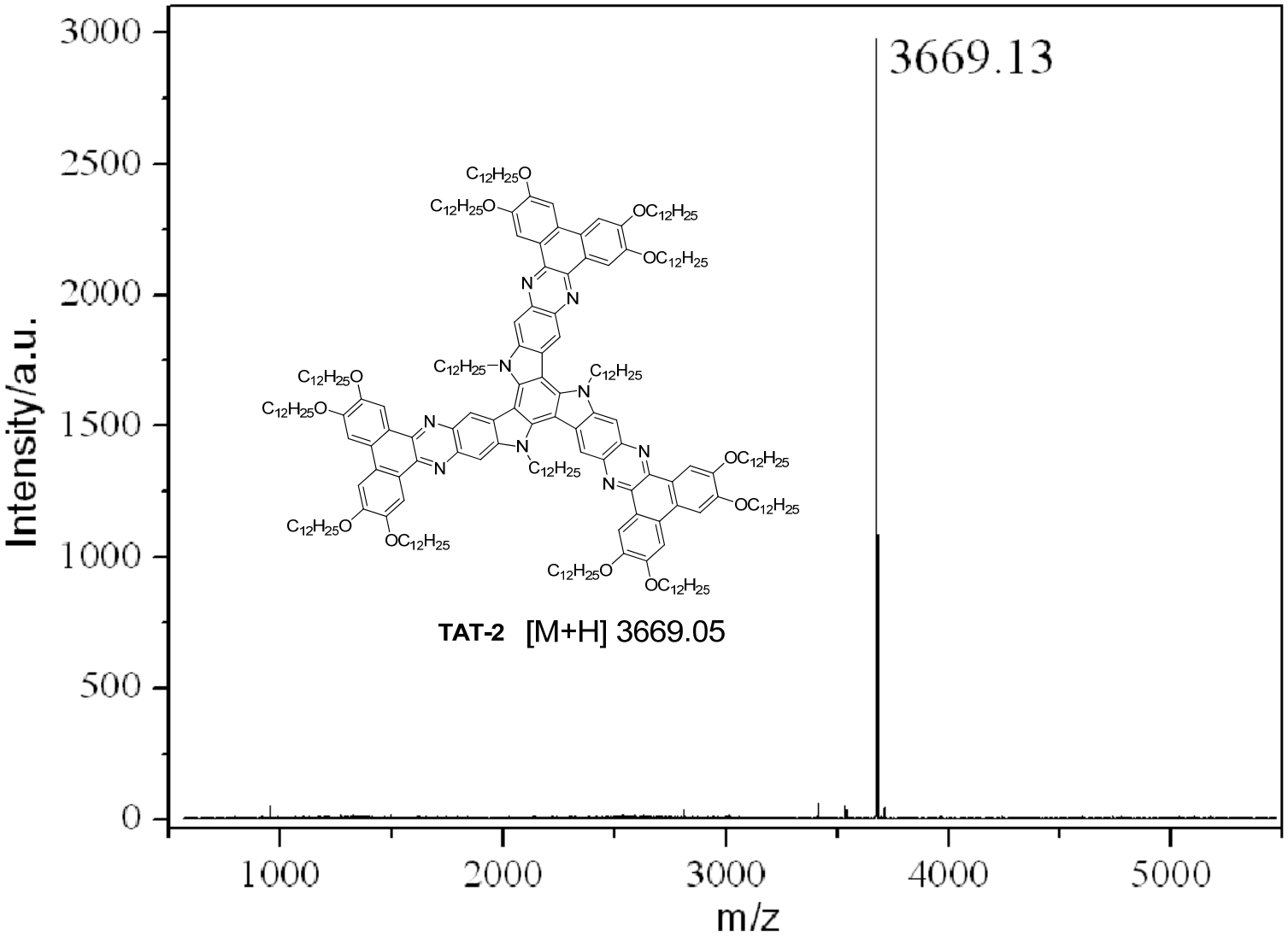


Figure S11: MALDI-TOF MS spectrum of **TAT-2**