Electonic Supplementary Information(ESI)

Synthesis and Characterization of Novel Symmetrical Two-photon Chromophores Derived from Bis(triphenylaminotetrathienoacenyl) and Fused-thiophene Units

Sureshraju Vegiraju,[a] Yi-You Liu,[b] Kumaresan Prabakaran,[a] Jen-Shyang Ni,[c] Hsien-Cheng Yu, [a] Shueh Lin Yau, [a] Jiann T. Lin,[a,c] Ming-Chou Chen,[a]* and Tzu-Chau Lin[b]*

[a] Department of Chemistry, National Central University, Jhongli 32001, Taiwan.

[b] Photonic Materials Research Laboratory, Department of Chemistry, National Central University, Jhongli 32001, Taiwan.

[c] Institute of Chemistry, Academia Sinica, Nankang 11529, Taipei, Taiwan.

* Correspondence and requests for materials should be addresed to

E-mail: mcchen@ncu.edu.tw,

E-mail: tclin@ncu.edu.tw,

1. **Two photon measurements**
2. **NMR and Mass spectra**
3. **Thermogravimetric analysis.**

1. Two-photon-excited fluorescence (2PEF) measurements

Two-photon-excited fluorescence spectra of the studied model fluorophore in solution phase (concentration: 1×10^{-4}M) were measured according to the protocol established by Xu and Webb using Fluorescein (0.1N NaOH solution) as the standard.[4] The experimental setup is illustrated in Figure S1.

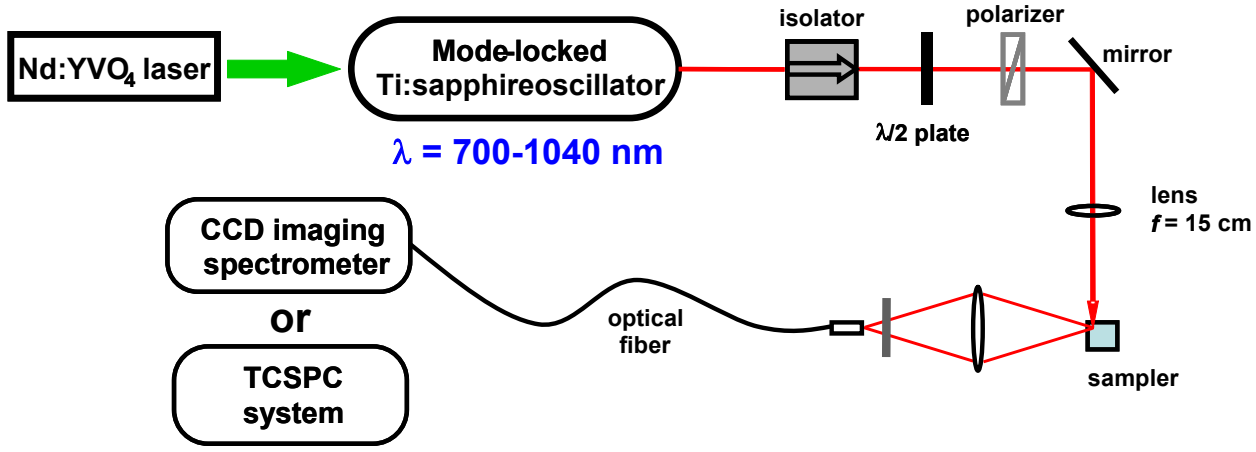

Figure S1. Optical setup for 2PEF-related experiments.

In brief, the excitation light source was a mode-locked Ti:Sapphire laser (Chameleon Ultra II, Coherent Inc.) which delivers ~140fs pulses with the repetition rate of 80MHz and the beam diameter of 2mm. The intensity level of the excitation beam was carefully controlled by the combination of a λ/2 wave plate and a polarizer in order to avoid the saturation of absorption and photodegradation. To minimize the effects of re-absorption, the excitation beam was focused as close as possible to the wall of the quartz cell (10mm×10mm cuvette) and the 2PEF emissions were collected and induced by a fiber bundle into a CCD imaging spectrometer (USB-4000, Ocean Optics) for the spectra recording. This optical system was also utilized for the characterization of the quadratic dependence of the 2PA-induced up-conversion emission intensity on the pumping intensity for every data point.

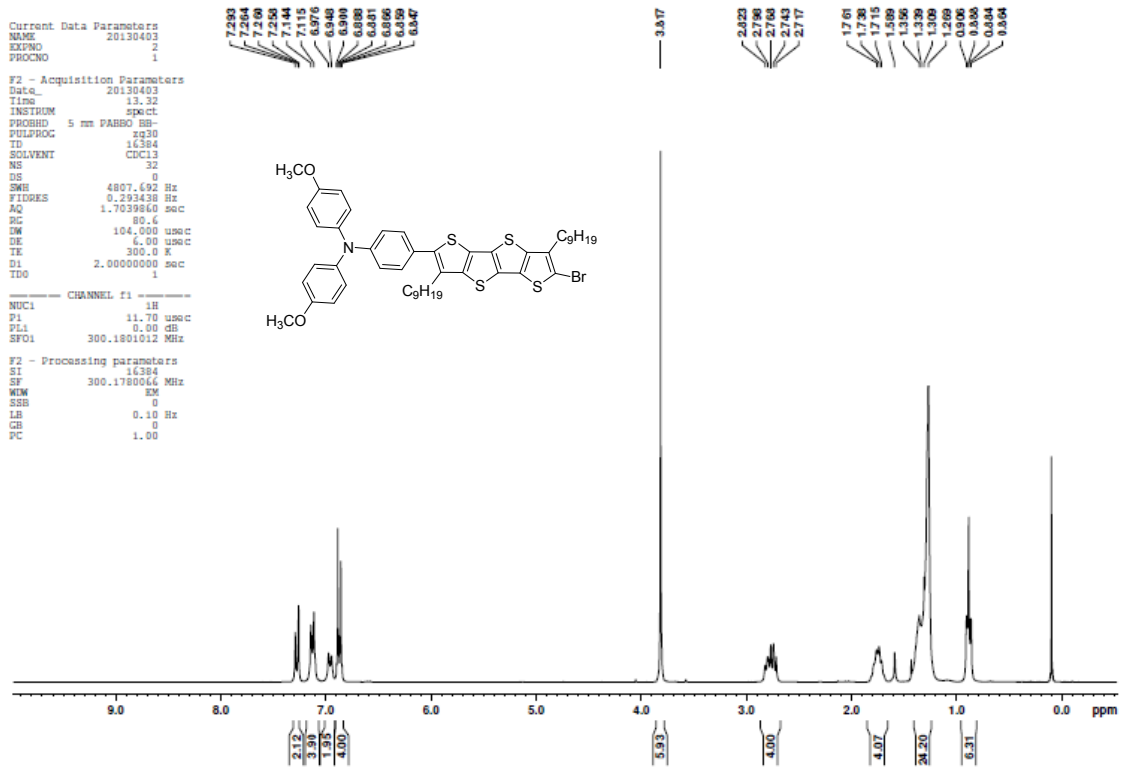

Figure S2. ^{1}H NMR (300 MHz, CDCl3) spectrum of compound **5.**

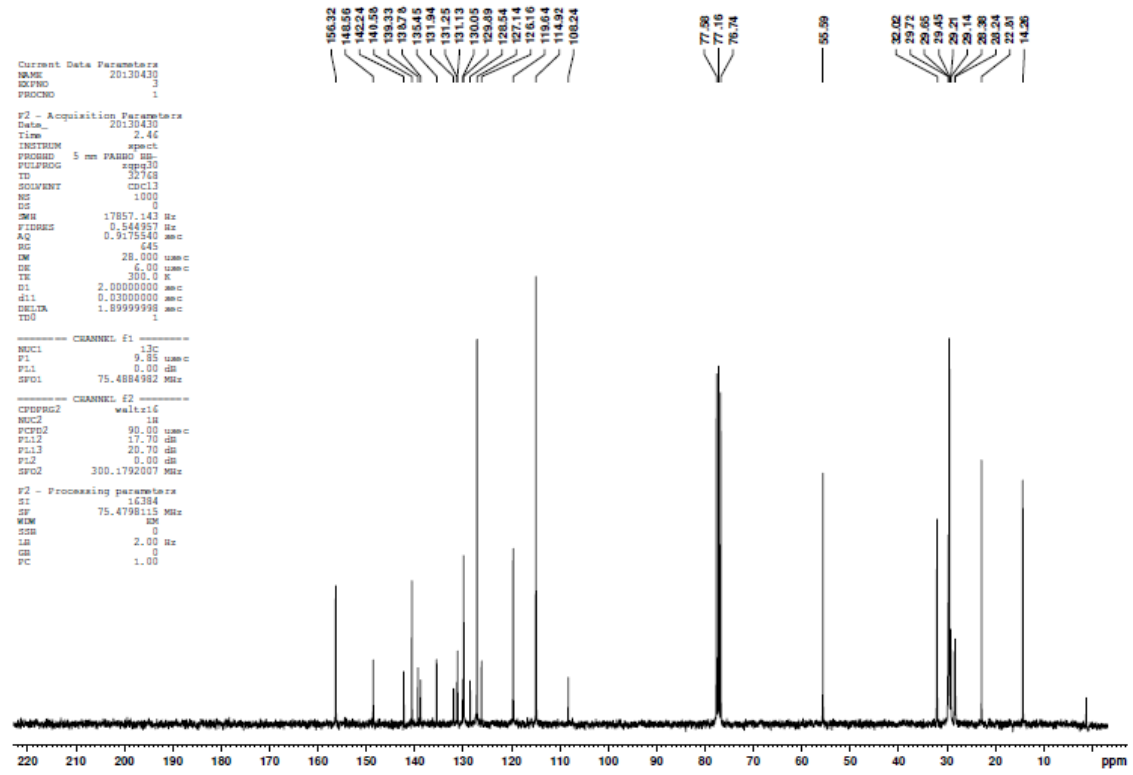

Figure S3. ^{13}C NMR (75 MHz, CDCl3) spectrum of compound **5.**

[Elemental Composition]
Data : 1020624-007
Sample: MTPA-TTAR2-Br
Note : HRFAB-885.2377
Inlet : Direct
RT : 2.73 min

Date : 24-Jun-2013 10:50

Ion Mode : FAB+
Scan#: 14

Elements : C 48/0, H 80/0, Br 1/0(79Br 1/0, 81Br 1/0), N 1/0, O 2/0, S 4/0
Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000
Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
885.2371	89.6	-0.7 / -0.6	25.0	C 48 H 56 79Br N O 2 S 4

Figure S4. HRMS of compound **5**.

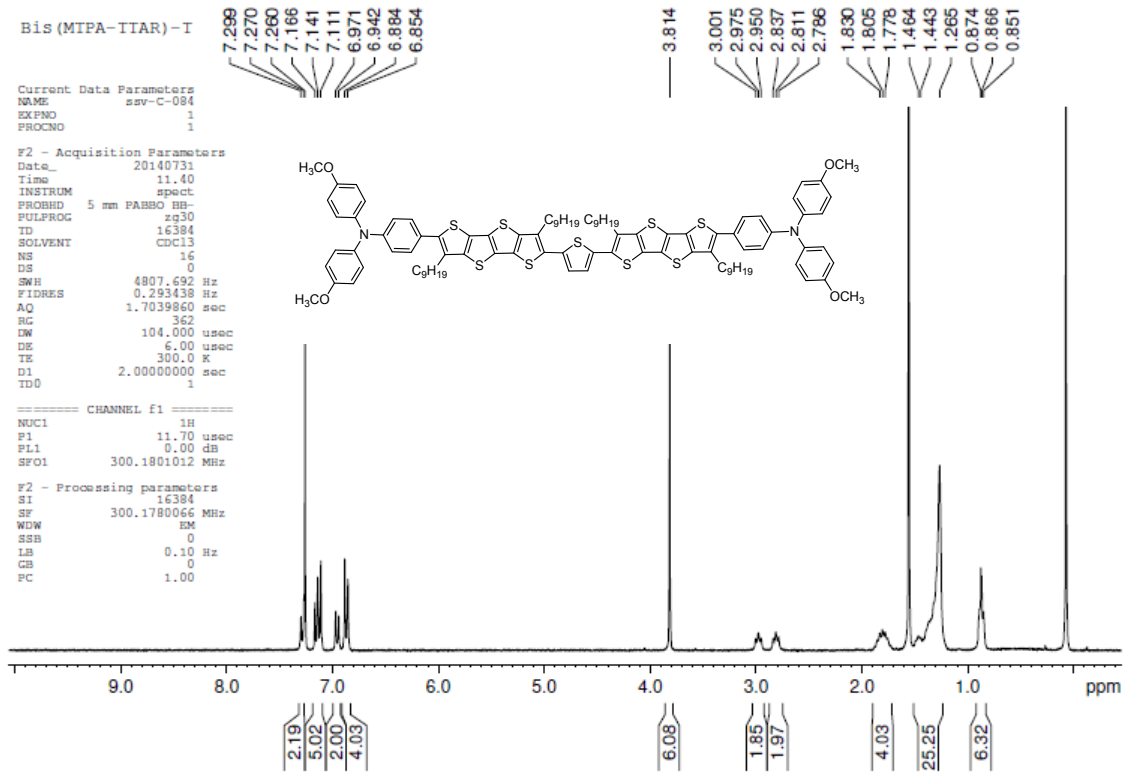

Figure S5. [1]H NMR (300 MHz, CDCl3) spectrum of compound **1.**

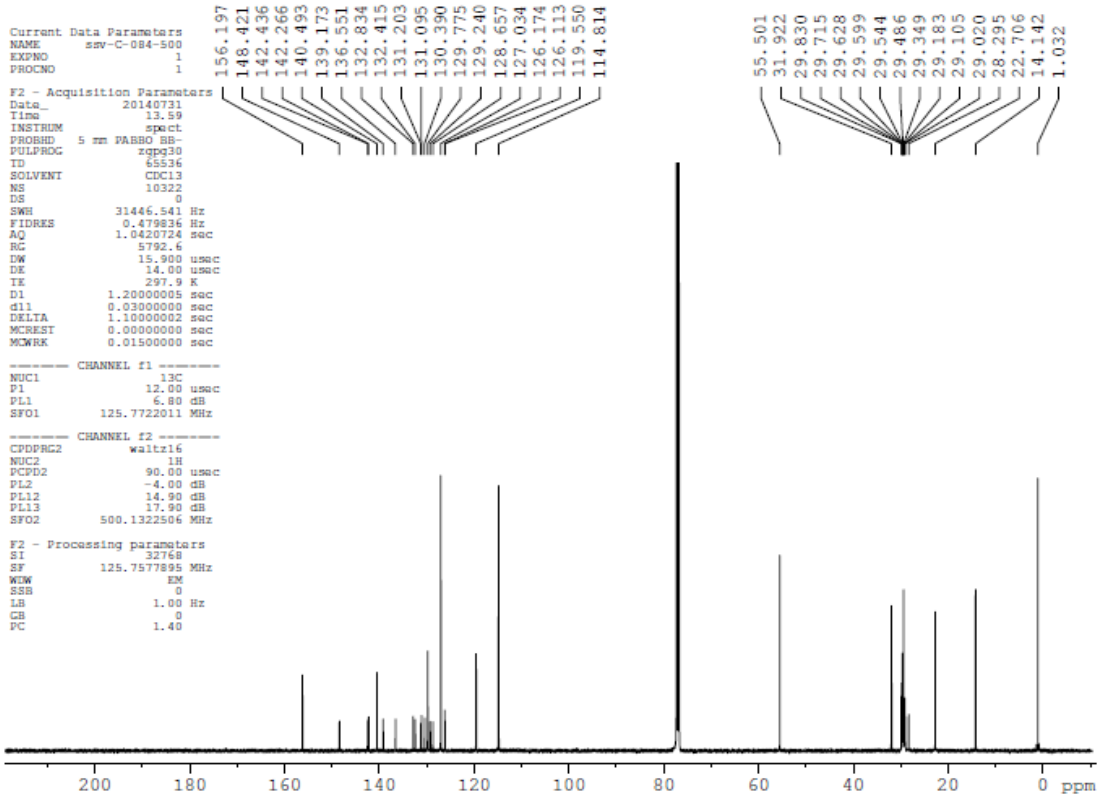

Figure S6. ^{13}C NMR (125 MHz, CDCl3) spectrum of compound **1.**

Page: 1

[Elemental Composition]
Data : 1031006-002
Sample: BISL(MTPA-TTAR)-T
Note : HRFAB-1694.6265
Inlet : Direct
RT : 2.00 min
Elements : C 100/0, H 200/0, N 2/0, O 4/0, S 9/0
Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000
Unsaturation (U.S.) : -0.5 - 200.0

Date : 06-Oct-2014 13:41

Ion Mode : FAB+
Scan#: 25

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1694.6260	20.0	-0.3 / -0.5	54.0	C 100 H 114 N 2 O 4 S 9

Figure S7. HRMS of compound **1**.

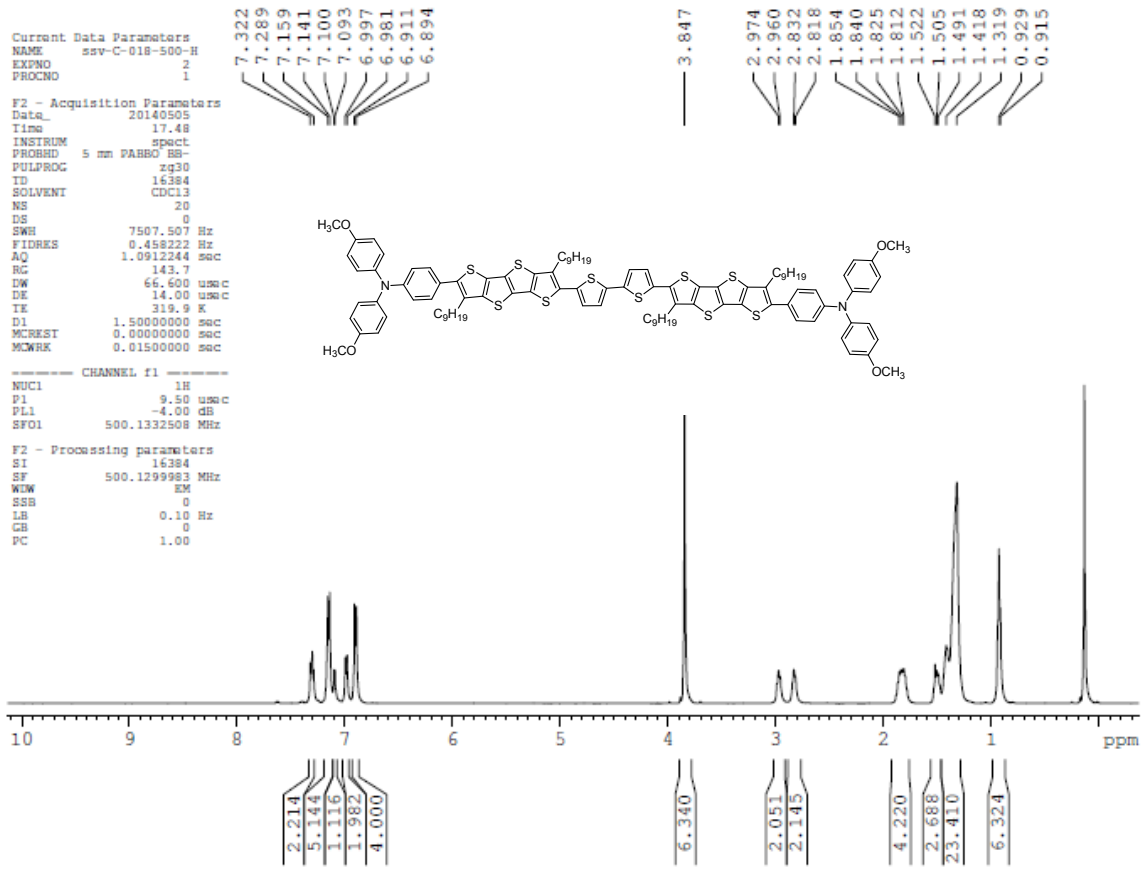

Figure S8. ^{1}H NMR (500 MHz, CDCl3) spectrum of compound **2.**

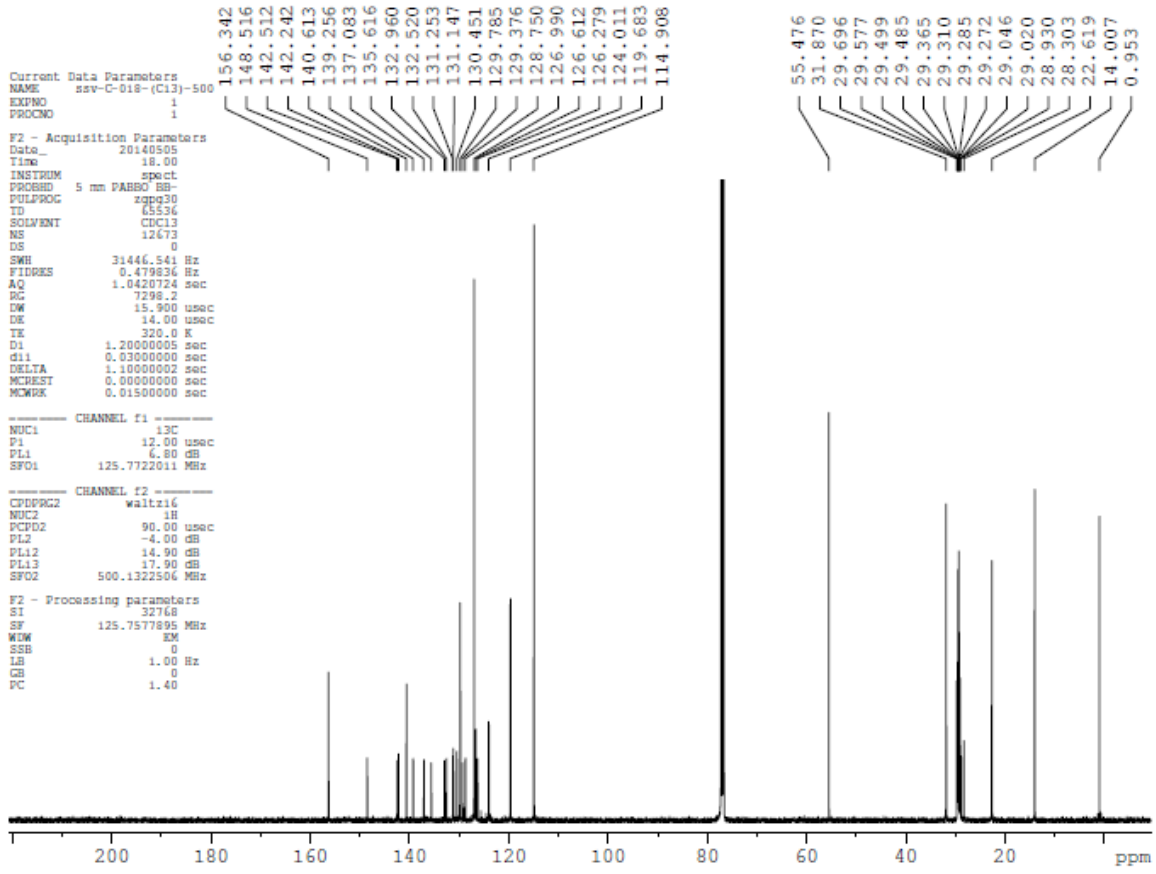

Figure S9. ^{13}C NMR (125 MHz, CDCl3) spectrum of compound **2.**

```
[ Elemental Composition ]                                          Page: 1
Data  : 1030407-005                    Date : 07-Apr-2014 11:49
Sample: Bis(MTPA-TTAR)-bT
Note  : HRFAB-1776.6142
Inlet : Direct                         Ion Mode : FAB+
RT : 2.60 min                          Scan#: 25
Elements : C 104/0, H 120/0, N 2/0, O 4/0, S 10/0
Mass Tolerance      : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000
Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
 1776.6161    12.5     +1.0 /  +1.9   58.0  C 104 H 116 N 2 O 4 S 10
```

Figure S10. HRMS of compound **2**.

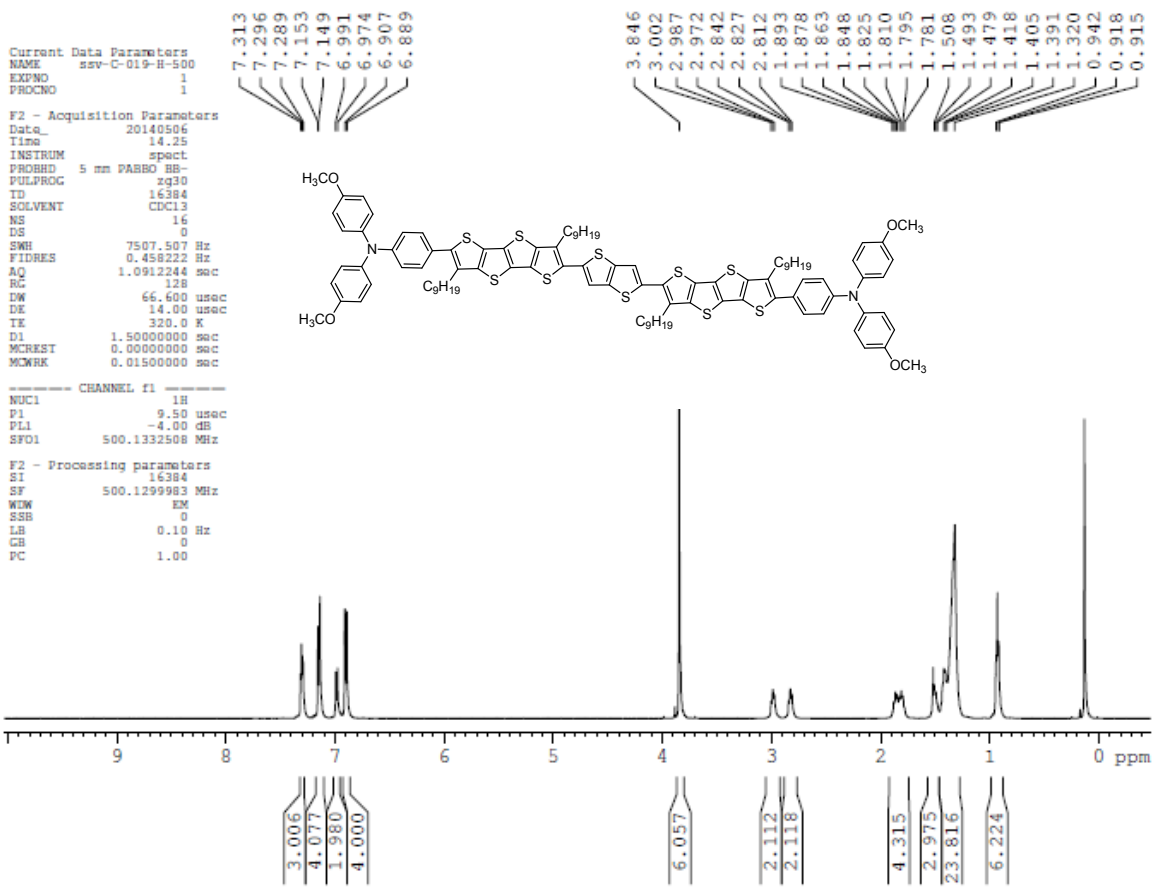

Figure S11. ^{1}H NMR (500 MHz, CDCl3) spectrum of compound **3.**

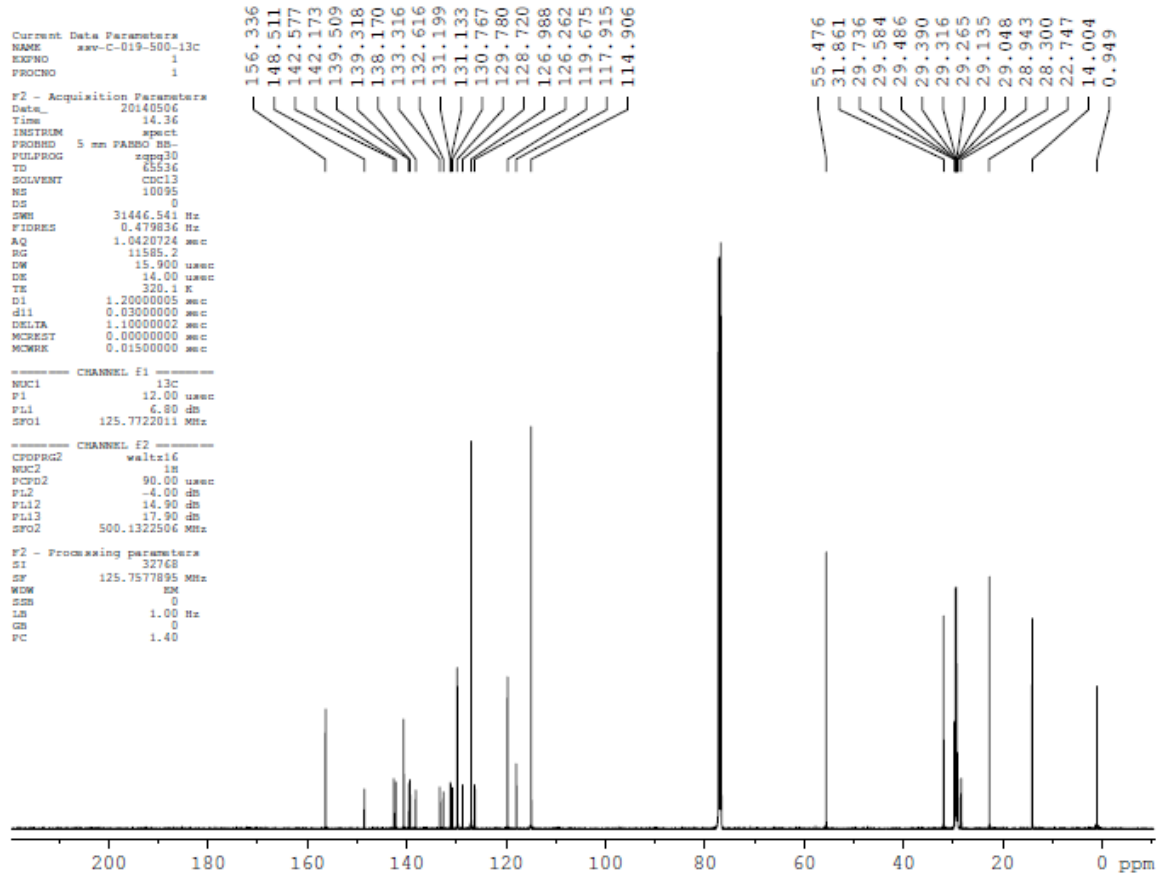

Figure S12. ^{13}C NMR (125 MHz, CDCl3) spectrum of compound **3.**

```
[ Elemental Composition ]                                          Page: 1
Data  : 1030407-006                    Date : 07-Apr-2014 13:55
Sample: Bis(MTPA-TTAR)-TT
Note : HRFAB-1750.5986
Inlet : Direct                         Ion Mode : FAB+
RT : 2.92 min                          Scan#: 28
Elements : C 102/0, H 120/0, N 2/0, O 4/0, S 10/0
Mass Tolerance      : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000
Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
 1750.5974    18.2     -0.7 /  -1.2   57.0  C 102 H 114 N 2 O 4 S 10
```

Figure S13. HRMS of compound **3**.

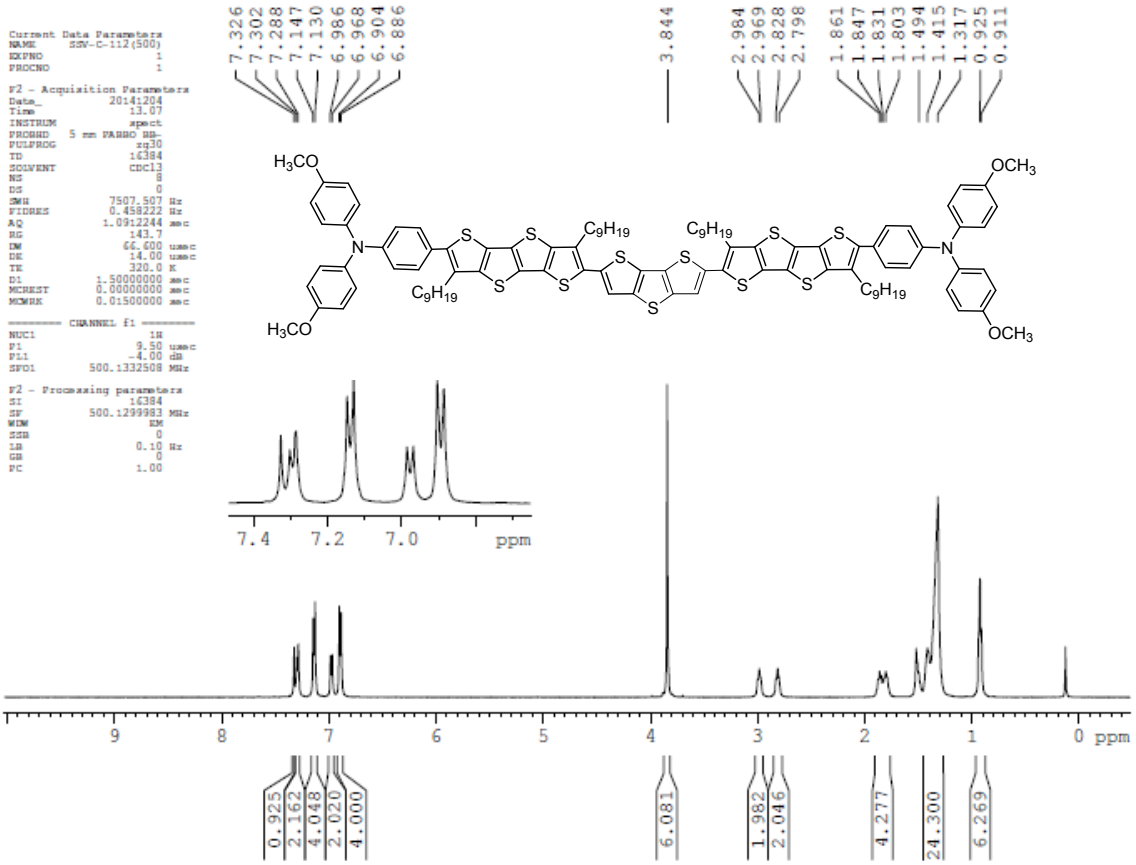

Figure S14. ^{1}H NMR (500 MHz, CDCl3) spectrum of compound **4.**

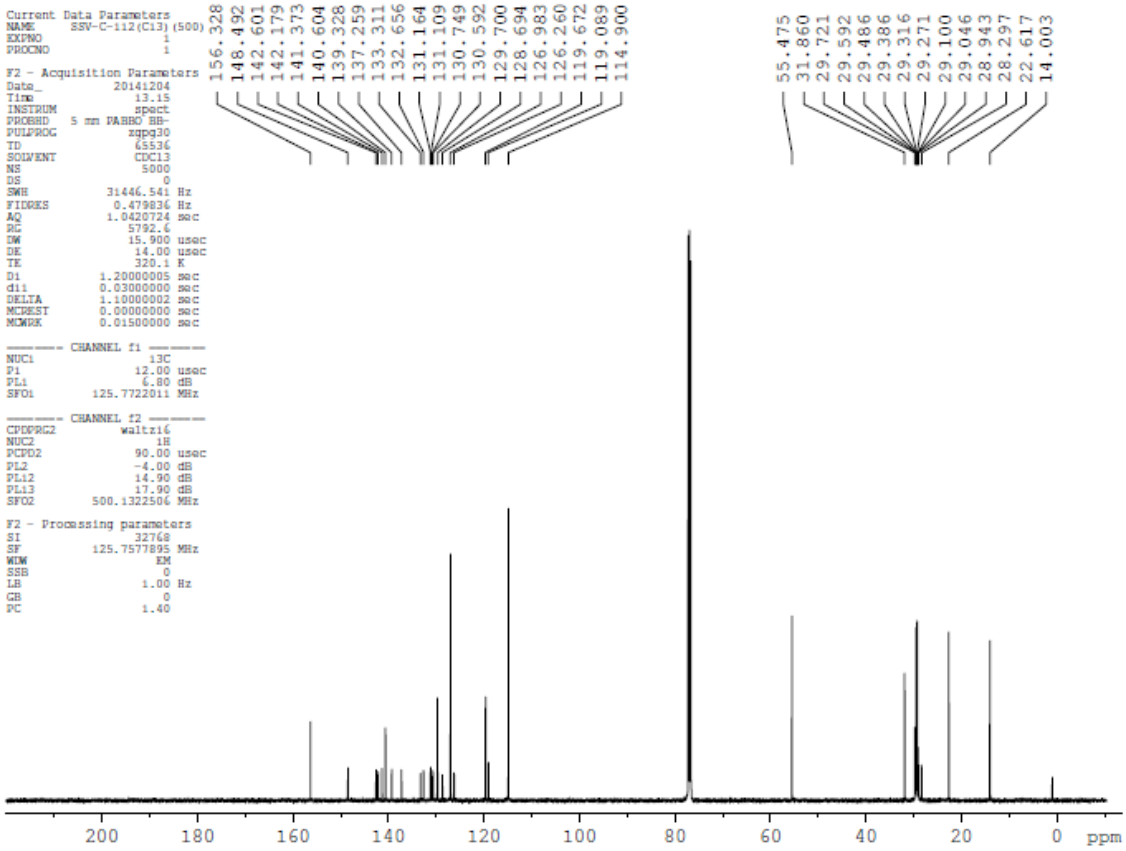

Figure S15. ^{13}C NMR (125 MHz, CDCl3) spectrum of compound **4.**

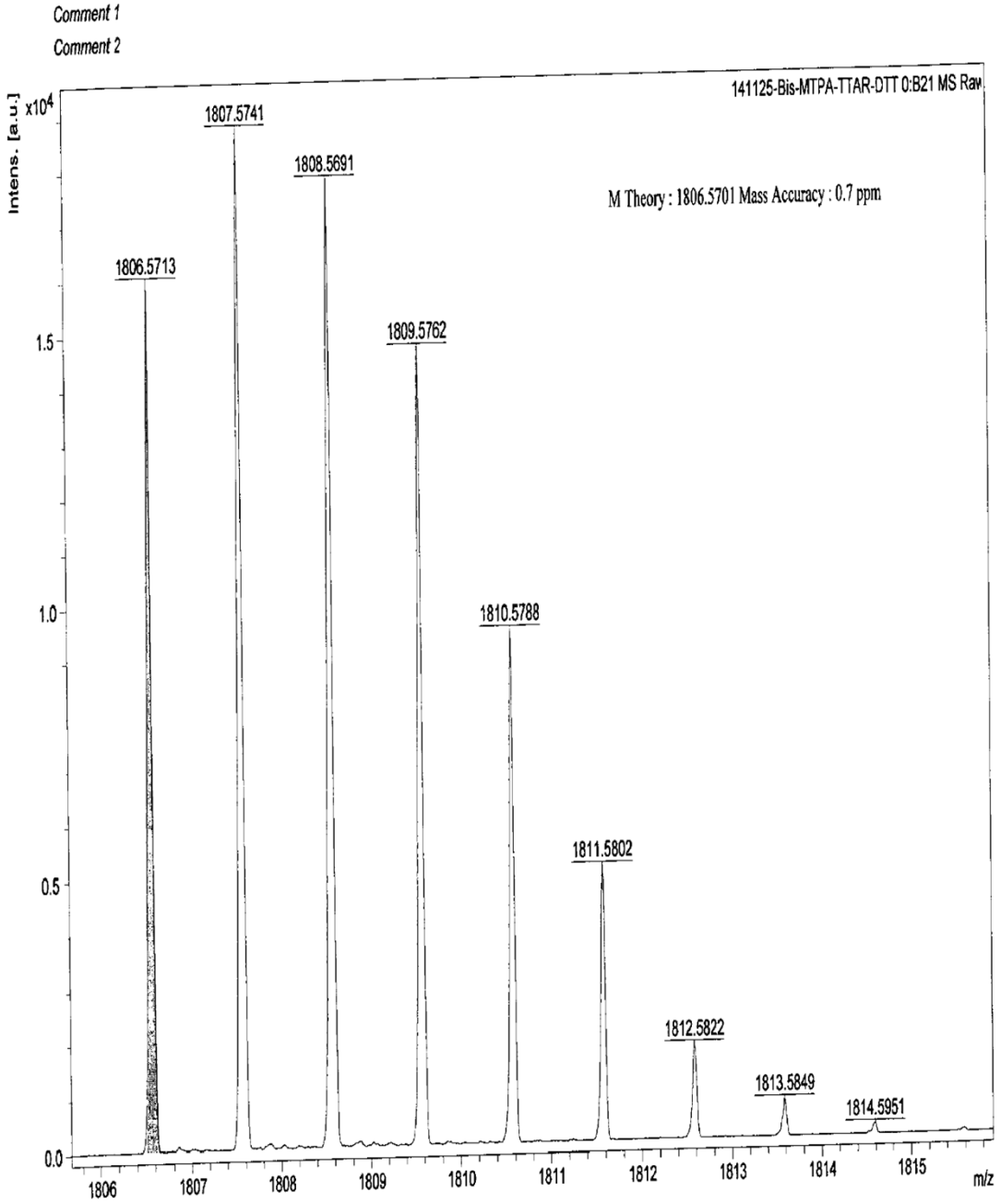

Figure S16. ESI-MS spectrum of compound **4.**

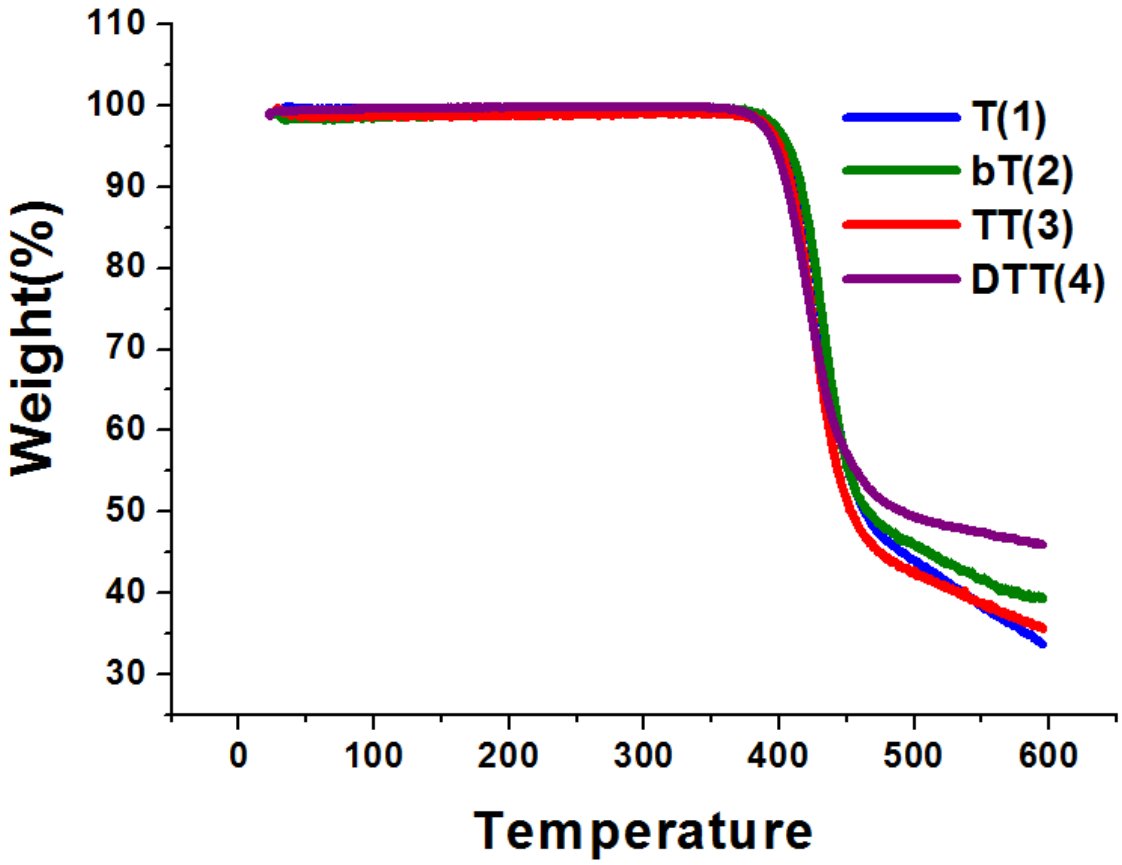

Figure S17. Thermogravimetric Analysis of compounds **1**-**4**.