Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information for

## Regio- and Stereo-Selective [4+4] Photodimerization of Angular-shaped Dialkyltetracenedithiophene

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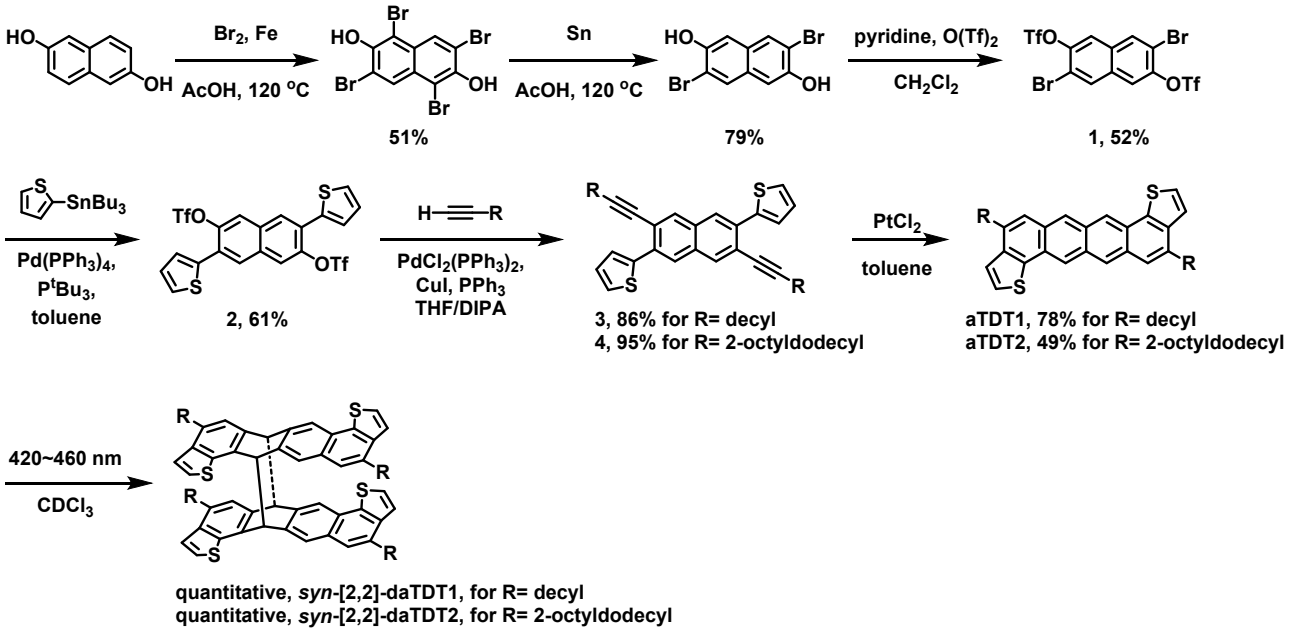
## 1. General remarks

All chemicals were obtained from commercial sources and used as received unless otherwise specified. Anhydrous toluene was obtained from a SD-300 solvent purification system (AsiaWong Enterprise). $^{1}H$ and $^{13}C$ NMR spectra were measured using Agilent 400-MR DD2 (400MHz) or Agilent VNMRS600 (600 MHz) instrument spectrometers. Chemical shifts ($\delta$ values) are reported in ppm with respect to $CHCl_3$ ($\delta$ = 7.26 ppm for $^{1}H$ NMR and $\delta$ = 77 ppm for $^{13}C$ NMR). Coupling constants (J) are given in Hz. $^{13}C$ NMR was proton broad-band-decoupled. Multiplicities of peaks are denoted by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution molecular weight was determined by a high resolution gas chromatograph mass spectrometer (type: AccuTOF GCX, JEOL) at the center of advanced instrumentation, National Chiao Tung university. Heteronuclear single quantum coherence (HSQC) spectroscopy, heteronuclear multiple bond correlation (HMBC) spectroscopy, rotating-frame nuclear Overhauser effect correlation spectroscopy (ROESY), National Chiao Tung university with Agilent VNMRS600 spectrometers. Absorption spectra were collected with a Hitachi U-4100 UV/Vis spectrophotometer. Fluorescence spectra were recorded with a Horiba FluoroMax 4 spectrometer. Mass spectra are collected with JEOL AccuTOF GCX High Resolution Gas Chromatograph Mass Spectrometer. X-ray crystal structure of **aTDT1** was determined by the instrumentation center, National Tsing Hua University with a single-crystal diffractometer (type: Bruker APEX DUO).

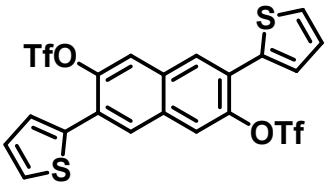
## 2. Synthetic details

**Scheme S1** Synthetic route to ***syn*-[2,2]daTDT**




1,3,5,7-tetrabromo-2,6-dihydroxynaphthalene, 1,5-dibromo-2,6-dihydroxynaphthalene, 3,7-dibromo-2,6-bis(trifluoromethanesulfonyloxy)naphthalene were synthesized based on the reported procedures.[1]

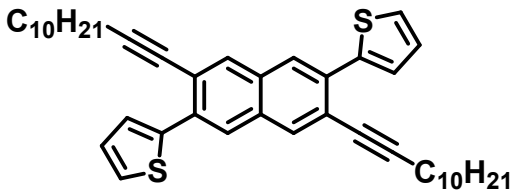
**Synthesis of 3,7-di(thiophen-2-yl)naphthalene-2,6-diyl bis(trifluoromethanesulfonate)**




A solution of 3,7-dibromonaphthalene-2,6-diyl bis(trifluoromethanesulfonate) (1.75 g, 3.0 mmol), tributyl(thiophen-2-yl)stannane (2.24 g, 6.0 mmol) in toluene (50 mL) was degassed under nitrogen for 1 h. $Pd(PPh_3)_4$ (174 mg, 0.15 mmol) and tri-*tert*-butylphosphine (31 mg, 0.15 mmol) was added and the mixture was stirred at 120 °C for 12 h, quenched with water (50 mL), and extracted with ethyl acetate (100 mL). The combined organic layer was washed with brine solution (100 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under

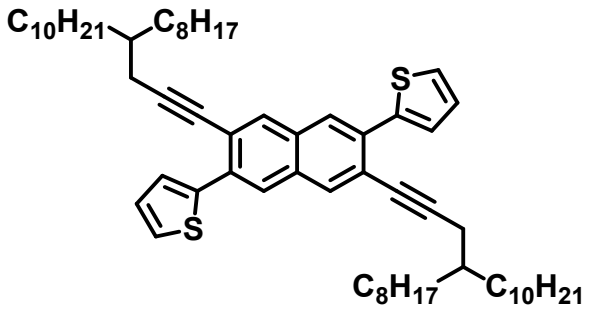
vacuum and the residue was washed by MeOH. Recrystallization from MeOH furnished 3,7-di(thiophen-2-yl)naphthalene-2,6-diyl bis(trifluoromethanesulfonate) **2** as a white solid (1.09 g, yield: 61%). $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.09 (s, 2 H), 7.91 (s, 2 H), 7.51 (d, $J$ = 4.8 Hz, 2 H), 7.48 (d, $J$ = 3.2 Hz, 2 H), 7.19 (dd, $J$ = 4.8 Hz, $J$ = 3.2 Hz, 2 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 145.77, 135.66, 131.23, 130.38, 128.74, 128.34, 128.10, 127.77, 123.26, 120.22, 120.07, 116.88, 113.68; HRMS (FD, $C_{20}H_{10}O_6F_6S_4^{+\cdot}$): calcd, 587.9258; found, 587.9256.

**Synthesis of 2,2'-(3,7-di(dodec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene**



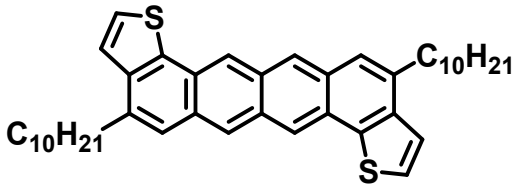

To a mixture of 3,7-di(thiophen-2-yl)naphthalene-2,6-diyl bis(trifluoromethanesulfonate) **2** (450 mg, 0.76 mmol), dodec-1-yne (350 mg, 1.6 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.15 mmol), CuI (40 mg, 0.15 mmol), and triphenylphosphine (53 mg, 0.15 mmol) was added THF/diisopropylamine (20 mL/20 mL) degassed by nitrogen. The mixture was then stirred for 8 h, quenched with water (30 mL), and extracted with ethyl acetate (100 mL). The combined organic layer was washed with brine solution (100 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under vacuum and the residue was purified by column chromatography (hexane:ethyl acetate=30:1). Recrystallization from MeOH furnished 2,2'-(3,7-di(dodec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene **3** as a white solid (410 mg, yield: 86%). $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.97 (s, 2 H), 7.86 (s, 2 H), 7.64-7.65 (m, 2 H), 7.37 -7.38 (m, 2 H), 7.11-7.13 (m, 2 H), 2.45 (t, $J$ = 7.2 Hz, 4 H), 1.58-1.64 (m, 4 H), 1.41-1.45 (m, 4 H), 1.26–1.28 (m, 24 H), 0.88 (t, $J$ = 6.8 Hz, 6 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): 142.0, 133.4, 133.2, 131.1, 127.1, 127.0, 126.8, 125.7, 121.0, 95.9, 80.3, 31.9, 29.6, 29.55, 29.3, 29.2, 29.0, 28.4, 22.7, 19.8, 14.1; HRMS (EI, $C_{42}H_{52}S_2^{+\cdot}$): calcd, 620.3505; found, 620.3491.

**Synthesis of 2,2'-(3,7-bis(4-octyltetradec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene**



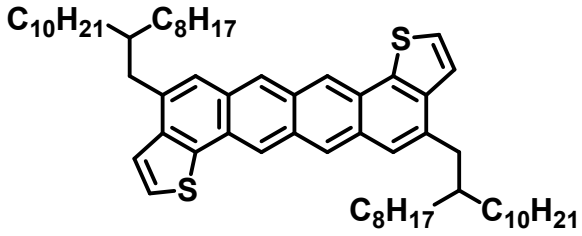

To a mixture of 3,7-di(thiophen-2-yl)naphthalene-2,6-diyl bis(trifluoromethanesulfonate) **2** (225 mg, 0.38 mmol), 9-(prop-2-yn-1-yl)nonadecane (338 mg, 0.84 mmol), $Pd(PPh_3)_2Cl_2$ (71 mg, 0.1 mmol), CuI (20 mg, 0.76 mmol), and triphenylphosphine (27 mg 0.76 mmol) was added THF/diisopropylamine (13 mL/13 mL) degassed by nitrogen. The mixture was then stirred for 8 h, quenched with water (30 mL), and extracted with ethyl acetate (100 mL). The combined organic layer was washed with brine solution (100 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under vacuum and the residue was purified by column chromatography (hexane:ethyl acetate=30:1). Recrystallization from MeOH furnished 2,2'-(3,7-bis(4-octyltetradec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene **4** as a white solid (327 mg, yield: 95%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.98 (s, 2 H), 7.87 (s, 2 H), 7.65 (d, $J$ = 3.6 Hz, 2 H), 7.37 (d, $J$ = 5.2 Hz, 2 H), 7.12 (dd, $J$ = 5.2 Hz, $J$ = 3.6 Hz, 2 H), 2.45 (d, $J$ = 5.6 Hz, 4 H), 1.59-1.67 (m, 2 H), 1.18-1.49 (m, 64 H), 0.88 (t, $J$ = 6.4 Hz, 12 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 142.1, 133.4, 133.3, 131.1, 127.2, 127.0, 126.9, 125.7, 121.2, 94.7, 81.1, 37.23, 33.7, 32.0, 31.9, 30.0, 29.7, 29.7, 29.7, 29.4, 26.9, 24.1, 22.7, 14.1. ; HRMS (FD, $C_{62}H_{92}S_2^{+\cdot}$): calcd, 900.6635; found, 900.6622.

**Synthesis of aTDT1**




To a solution of 2,2'-(3,7-di(dodec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene **3** (200 mg, 0.322 mmol) in toluene (10 mL) was added $PtCl_2$ (8.6 mg, 0.0322 mmol). The mixture was stirred for 12 h at 110 °C, filtered with celite, and extracted by toluene. The solvent was removed under vacuum and the residue was recrystallized from toluene to give **aTDT1** as an orange solid (156 mg, yield: 78%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.81 (s, 2 H), 8.61 (s, 2 H), 7.60 (s, 2 H), 7.56 (s, 4 H), 3.04 (t, $J$ = 8.0 Hz, 4 H), 1.82-1.86 (m, 4 H), 1.27–1.49 (m, 28 H), 0.88 (s, $J$ = 7.0 Hz, 6 H); HRMS (EI, $C_{42}H_{52}S_2$): calcd, 620.3505; found, 620.3478. $^{13}$C NMR is not detected due to low solubility.

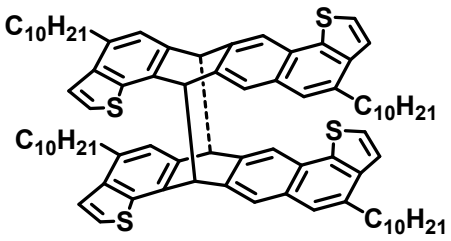
**Synthesis of aTDT2**




To a solution of 2,2'-(3,7-bis(4-octyltetradec-1-yn-1-yl)naphthalene-2,6-diyl)dithiophene **4** (200 mg, 0.22 mmol) in toluene (7 mL) was added $PtCl_2$ (5.9 mg, 0.022 mmol). The mixture was stirred for 12 h at 110 °C, filtered with celite, and extracted by toluene. The solvent was removed under vacuum and the residue was purified by column chromatography (hexane:ethyl acetate=30:1). Recrystallized from MeOH to give **aTDT2** as a yellow solid (98 mg, yield: 49%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.81 (s, 2 H), 8.61 (s, 2 H), 7.54 (s, 6 H), 2.94 (d, $J$ = 6.4 Hz, 4 H), 1.93-1.85 (m, 2 H), 1.44-1.18 (m, 64 H), 0.86-0.80 (m, 12 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 137.49, 137.25, 134.78,

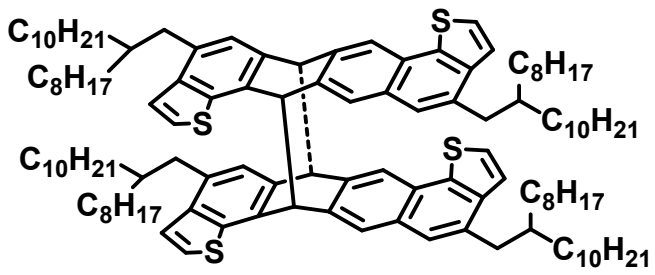
130.28, 129.99, 126.69, 126.04, 124.83, 124.46, 124.08, 120.78, 39.57, 38.18, 33.57, 31.90, 30.05, 29.65, 29.33, 26.59, 22.67, 14.10; HRMS (FD, $C_{62}H_{92}S_2^{+\cdot}$): calcd, 900.6635; found, 900.6642.

**Synthesis of *syn*-[2,2]-daTDT1**




A solution of **aTDT1** (10 mg, 0.016 mmol) in $CDCl_3$ (15 mL) was irradiated by a daylight lamp (3M, DL5000 OSRAM DULUX， 20W/800．50/60Hz．6000K) with a filter (Company: ROCOES; Product: P490/585, pink：$T_{ave}$>88% @ 610-700nm，$T_{ave}$>80% @ 420-460nm，$T_{ave}$<10% @ 520-550nm) and the mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum to afford quantitatively ***syn*-[2,2]-daTDT1** as a brown oil (10 mg, yield: 99 %).$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.11 (s, 2 H), 7.93 (s, 2 H), 7.53 (s, 4 H), 7.49 (s, 2 H), 7.46 (s, 4 H), 7.32 (s, 2 H), 6.42 (s, 2 H), 6.29 (s, 2 H), 3.01 (t, $J$ = 7.8 Hz, 4 H), 2.94 (t, $J$ = 7.6 Hz, 4 H), 1.74-1.77 (m, 4 H), 1.67-1.71 (m, 4 H), 1.25–1.38 (m, 56 H), 0.87 (t, $J$ = 6.8 Hz, 12 H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 139.1, 138.0, 137.8, 136.9, 135.4, 134.9, 134.4, 134.3, 130.4, 130.2, 126.9, 125.8, 125.1, 123.8, 123.2, 122.7, 122.6, 120.2, 118.1, 79.8, 78.0, 34.2, 34.1, 31.9, 30.9, 30.3, 29.61, 29.59, 29.54, 29.51, 29.3, 22.7, 14.1; HRMS (FD, $C_{84}H_{104}S_4^{+\cdot}$): calcd, 1240.7015; found, 1240.6997.

**Synthesis of *syn*-[2,2]-daTDT2**




A solution of **aTDT2** (10 mg, 0.011 mmol) in $CDCl_3$ (5 mL) was irradiated by a daylight lamp (3M, DL5000 OSRAM DULUX， 20W/800．50/60Hz．6000K) with a filter (Company: ROCOES; Product: P490/585, pink：$T_{ave}$>88% @ 610-700nm，$T_{ave}$>80% @ 420-460nm，$T_{ave}$<10% @ 520-550nm) and the mixture was stirred for 15 minutes at room temperature. The solvent was removed under vacuum to afford quantitatively ***syn*-[2,2]-daTDT2** as a brown oil (10 mg, yield: 99 %). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.12 (s, 2 H), 7.93 (s, 2 H), 7.52 (s, 4 H), 7.45 (s, 6 H), 7.28 (s, 2 H), 6.43 (s, 2 H), 6.29 (s, 2 H), 2.95-2.89 (m, 4 H), 2.89-2.82 (m, 4 H), 1.82-1.77 (m, 2 H), 1.75-1.69 (m, 2 H), 1.33-1.16 (m, 128 H) 0.89-0.81 (m, 24 H); HRMS (FD, $C_{124}H_{184}S_4^{+\cdot}$): calcd, 1801.3275; found, 1801.3260.

## 3. Time-dependent $^{1}$H NMR spectra of reversibility of *syn*-[2,2]-daTDT1

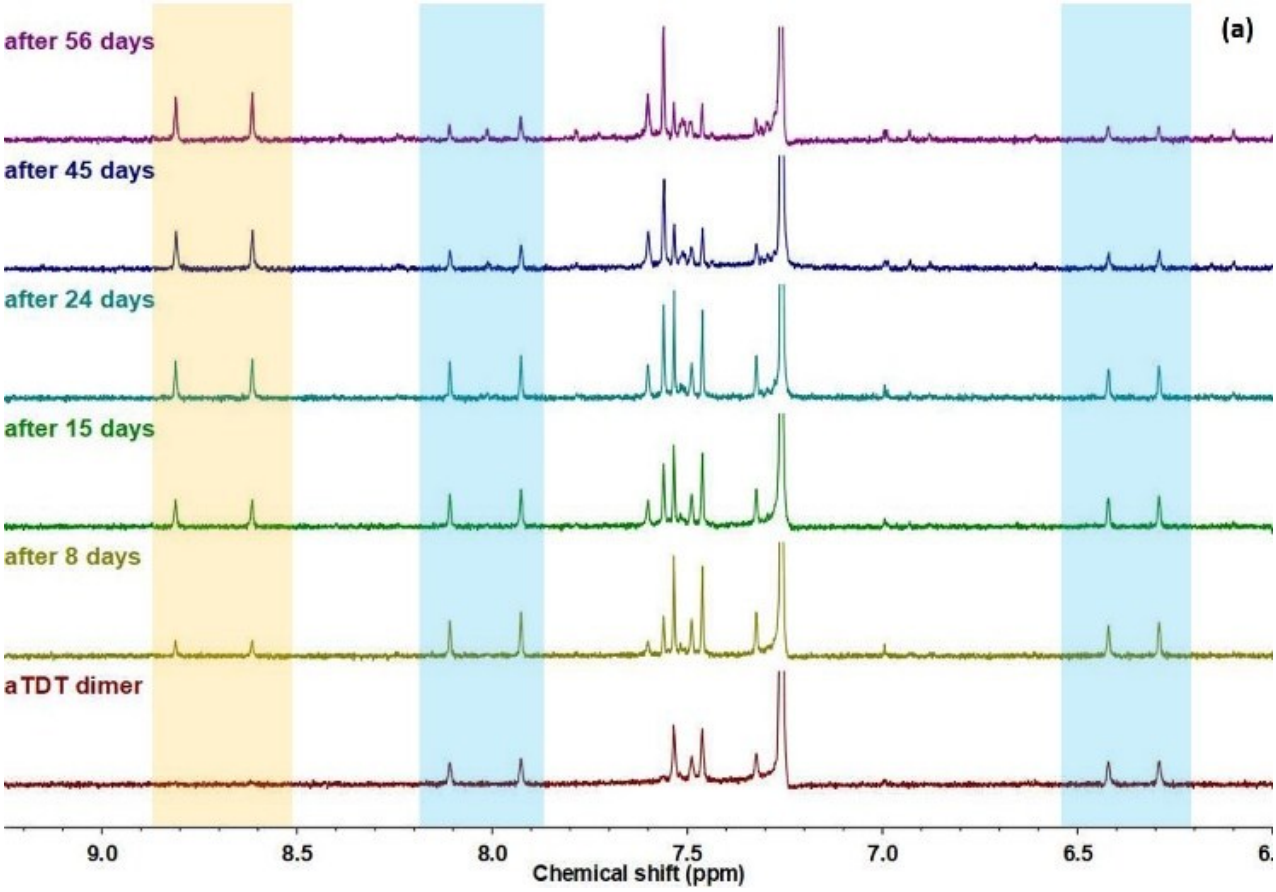
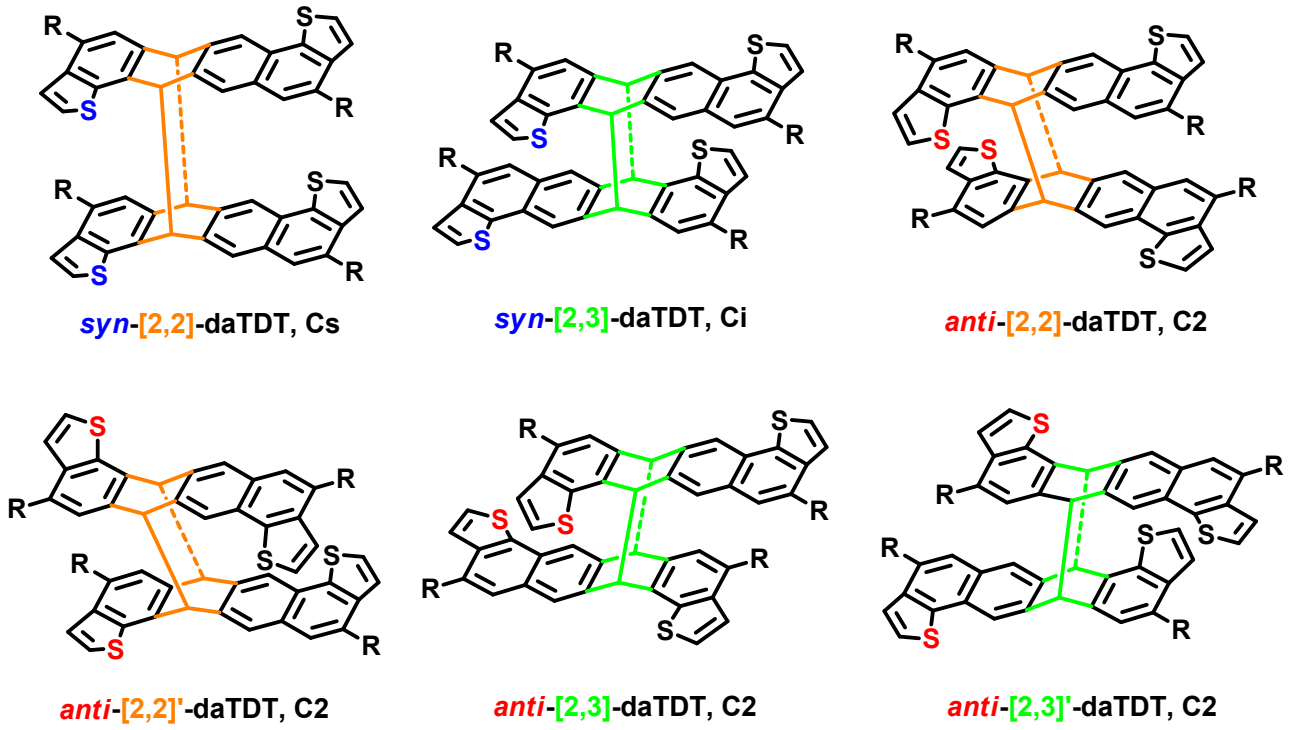



**Figure S1** Time-dependent $^{1}$H NMR spectra of reversibility of *syn*-[2,2]-daTDT1

## 4. Structural characterization of *syn*-[2,2]-daTDT by NMR spectroscopy

### 4.1. Possible isomers




**Scheme S2** Six possible stereoisomers and corresponding symmetry point groups for **daTDT**

### 4.2. Heteronuclear single quantum coherence (HSQC) spectroscopy to establish the one-bond C–H relations in daTDT1.

The HSQC spectrum of **daTDT1** is shown in **Figure S2**, in which 14 C–H correlations were found. Correlations- a", b", and e" arise from the phenyl and naphthalenyl moieties. Correlations- c" and d" result from the outmost thienyl groups. Correlations- f" and g" belong to the bridgehead C–H pairs. The rest are the C–H couplings related to the decanyl aliphatic side chains.

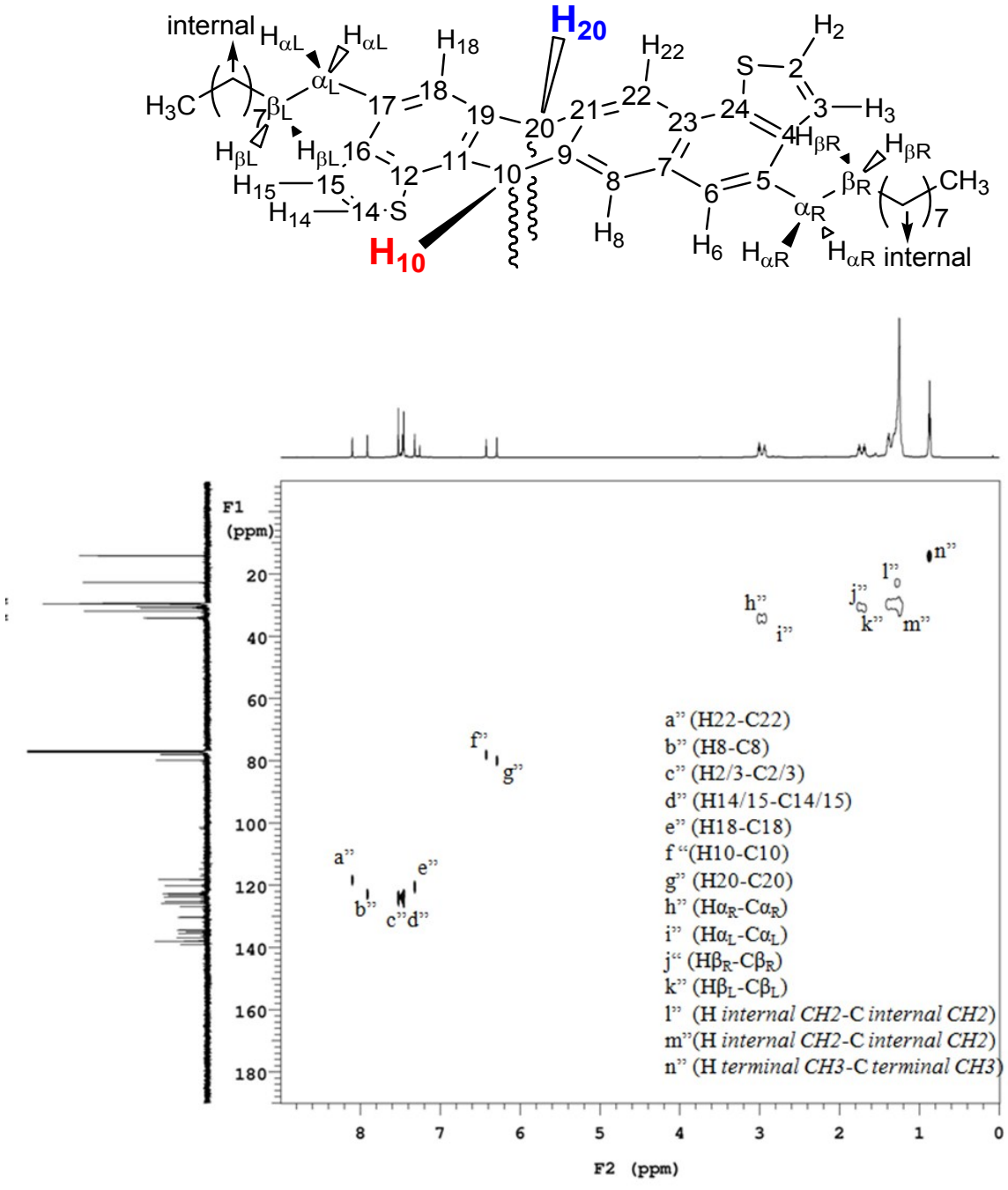



**Figure S2** HSQC spectrum of **daTDT1**.

### 4.3. Heteronuclear multiple bond correlation (HMBC) spectroscopy to establish the long-range C–H relations in daTDT1.

Magnified HMBC spectra of various regions are listed in **Figure S3**, **Figure S4**, **Figure S5**, **Figure S6**, and **Figure S7** respectively. In theory, $C_{20}$ would couple with $H_{22}$ and $H_{18}$ in HMBC spectroscopy and $C_{10}$ correlates with $H_8$. Based on this principle, $C_{10}$ and $C_{20}$ can be assigned accordingly (**Figure S3**, correlation A, B, and C). Moreover, the characterization of $H_{18}$ and $H_{22}$ is assisted by the statement that $C_{\alpha L}$ would couple with $H_{18}$ rather than $H_{22}$ (**Figure S7**, correlation Bx). In conjunction with the HSQC spectrum (**Figure S2**, correlation f", g", b", e", and a"), the NMR absorption peaks of $C_{10}/H_{10}$, $C_{20}/H_{20}$, $C_8/H_8$, $C_{18}/H_{18}$, and $C_{22}/H_{22}$ are determined.

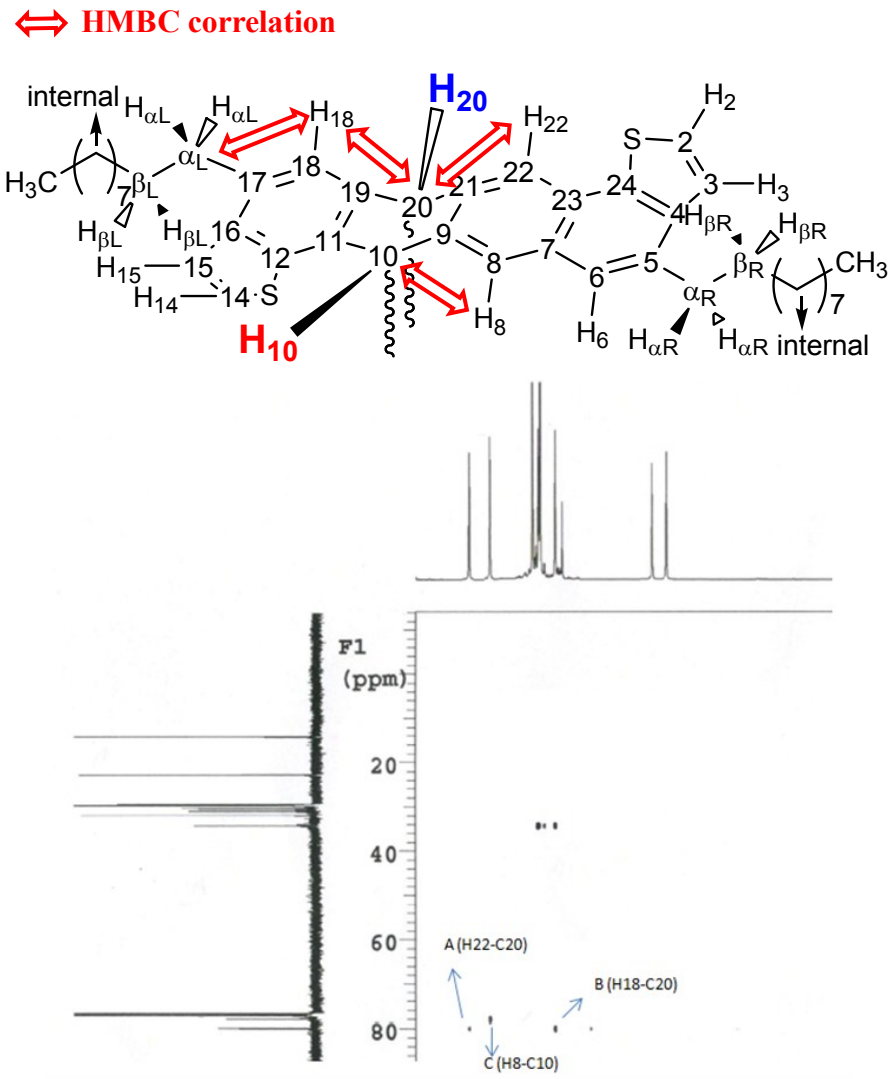



**Figure S3** Magnified HMBC spectrum of **daTDT1**

Subsequently, $C_{21}$ would couple with $H_{20}$ and $H_{22}$. The peak position of $C_{21}$ can thus be confirmed (**Figure S4**, correlation D and E). Similarly, $C_{19}$ would couple with $H_{18}$ and $H_{20}$ and $C_{19}$ is then located (**Figure S4**, correlation F and G). $C_9$ would couple with $H_8$ and $H_{10}$ and the chemical shift of $C_9$ can be verified (**Figure S4**, correlation H and I). $H_{10}$ would couple with $C_9$ and $C_{11}$. Since the position of $C_9$ is identified, the other correlation should be $H_{10}$–$C_{11}$ (**Figure S4**, correlation J). The recognition of $C_{11}$ is accomplished.

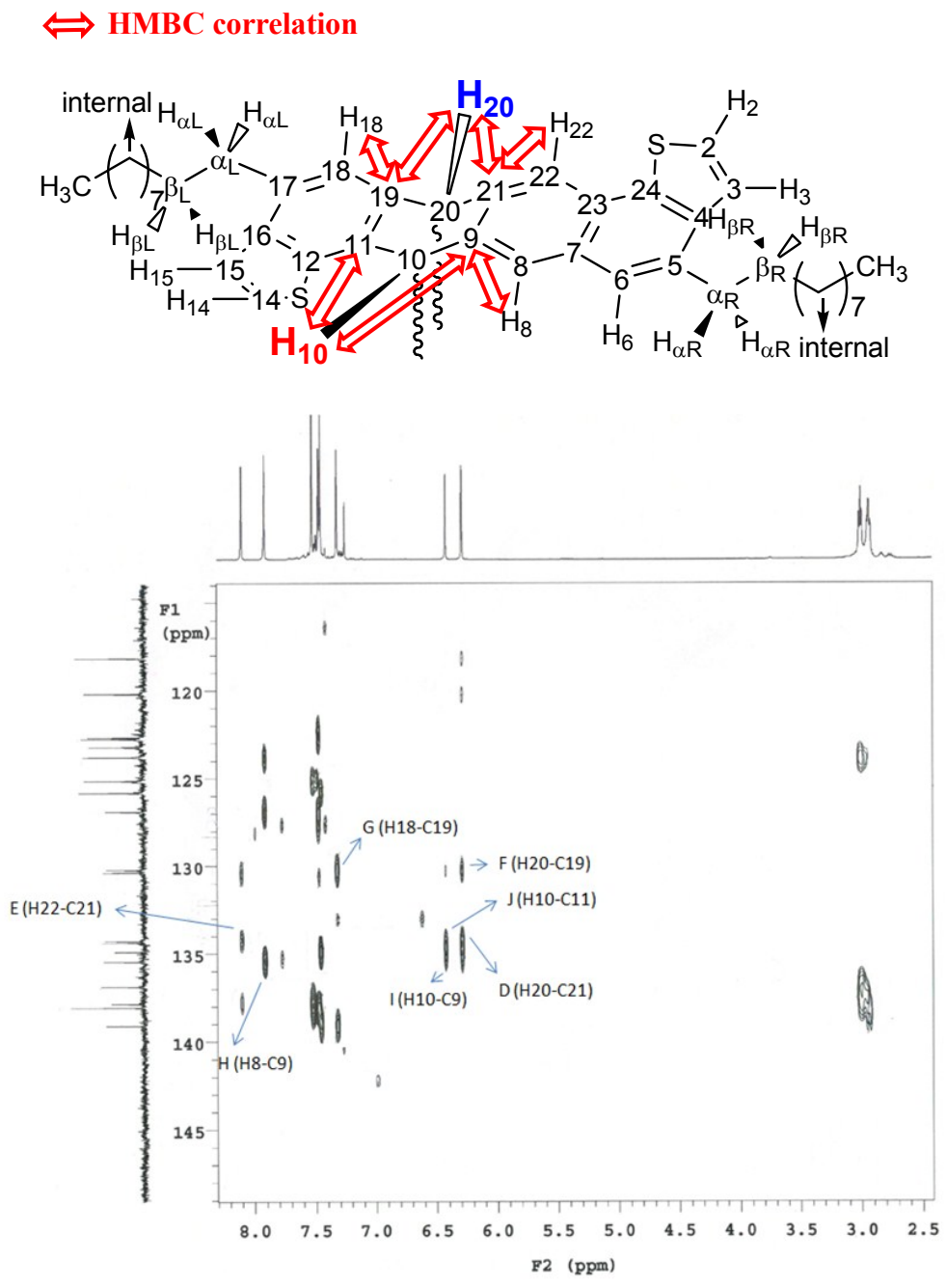



**Figure S4** Magnified HMBC spectrum of **daTDT1**.

As shown in **Figure S5**, searching along the vertical direction of correlation H ($H_8$–$C_9$), correlation K and L are found. They should correspond to $H_8$–$C_7$ and $H_8$–$C_6$. Correlation M ($H_{\alpha R}$–$C_6$) and L are linked to the same carbon, which is assigned as $C_6$. Therefore, one can deduce that K is $H_8$–$C_7$ and L is $H_8$–$C_6$. Following a similar strategy, correlation N and O are detected along the perpendicular line of E ($H_{22}$–$C_{21}$). N and O are $H_{22}$–$C_{23}$ and $H_{22}$–$C_{24}$ couplings. Correlation P ($H_6$–$C_{23}$) and N are associated with the same carbon, which is designated $C_{23}$. Since N is the $H_{22}$–$C_{23}$ signal, $C_{24}$ can thus be identified.

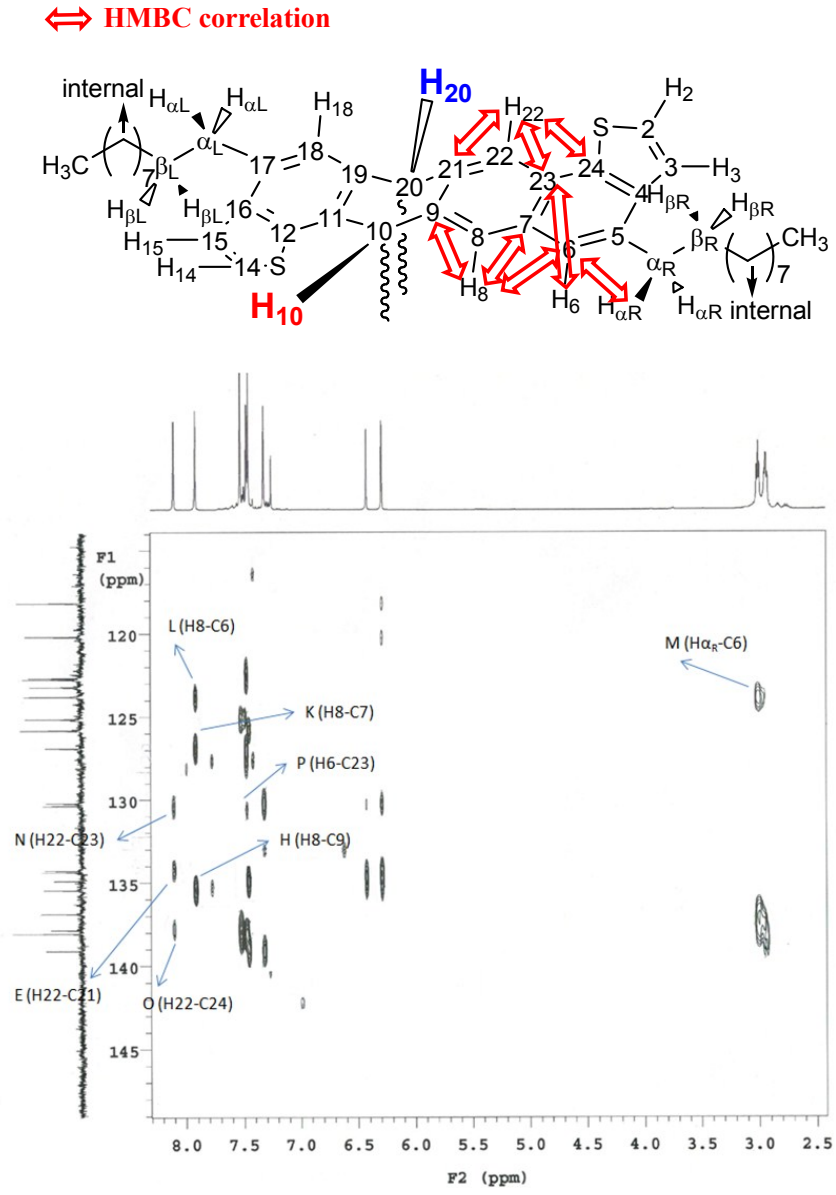



**Figure S5** Magnified HMBC spectrum of **daTDT1**.

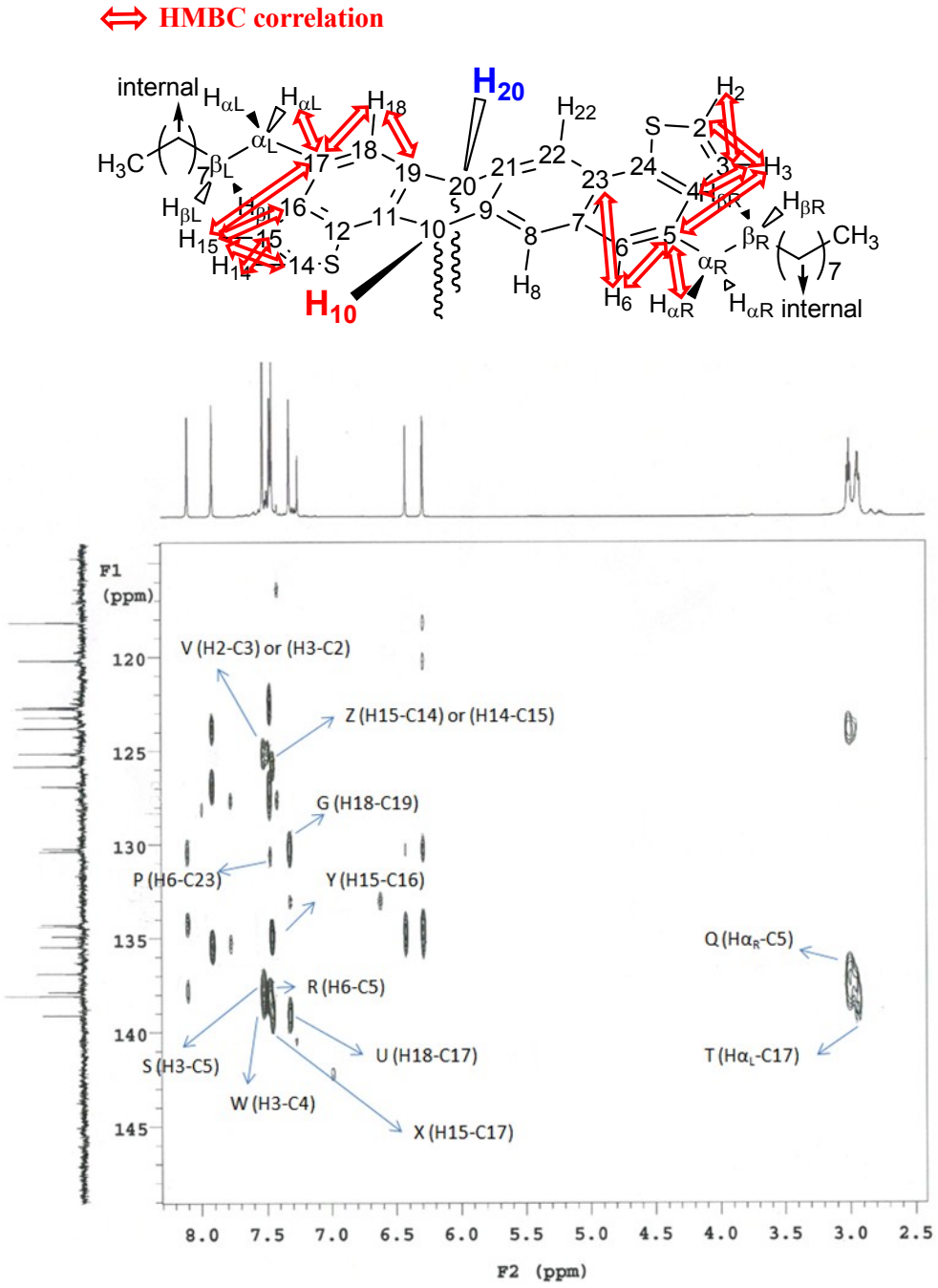



**Figure S6** Magnified HMBC spectrum of **daTDT1**.

In **Figure S6**, one can use $H_{\alpha R}$ to label $C_5$ via correlation Q ($H_{\alpha R}$–$C_5$). Q, R, and S are located at the same horizontal line, suggesting that the protons all relate to $C_5$. Through connecting P ($H_6$–$C_{23}$) and R ($H_6$–$C_5$), the identity of S should be $H_3$–$C_5$. In association with the HSQC spectrum (**Figure S2**, correlation c"), one can then infer that V is $H_3$-$C_2$ or $H_2$-$C_3$ and W is $H_3$-$C_4$. Furthermore, T ($H_{\alpha L}$–$C_{17}$) is used to identify $C_{17}$, which can then be employed to find correlation U and X relating to $C_{17}$. The signal G ($H_{18}$–$C_{19}$) can differentiate U ($H_{18}$–$C_{17}$) and X ($H_{15}$–$C_{17}$). The identification of

$H_{15}$ together with the HSQC spectrum (**Figure S2**, correlation d"), Z ($H_{15}$–$C_{14}$ or $H_{14}$–$C_{15}$) and Y ($H_{15}$–$C_{16}$) are recognized. There is still one aromatic carbon not being characterized. By eliminating all other possibilities, it should be $C_{12}$ at 137 ppm.

The proton and carbon ($H_{\alpha R}$, $C_{\alpha R}$, $H_{\beta R}$, $C_{\beta R}$, $H_{\alpha L}$, $C_{\alpha L}$, $H_{\beta L}$, $C_{\beta L}$, $H_{internal}$, $C_{internal}$, $H_{terminal}$, and $C_{terminal}$) absorptions in the aliphatic region can be easily assigned. The assignment is summarized in **Figure S7**.

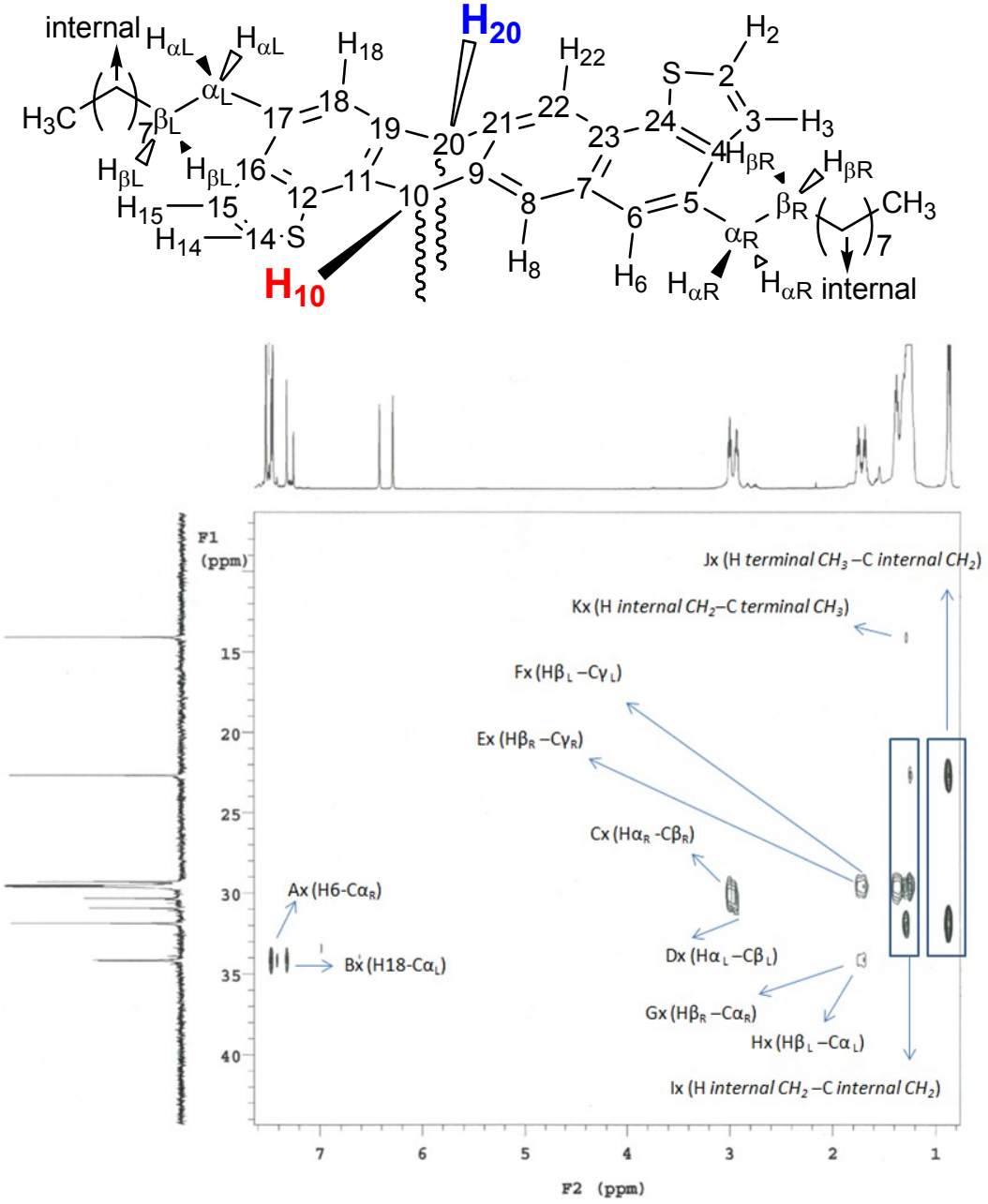



**Figure S7** Magnified HMBC spectrum of **daTDT1**

## 4.4. Rotating-frame nuclear Overhauser effect correlation spectroscopy (ROESY) of aTDT1 and daTDT2

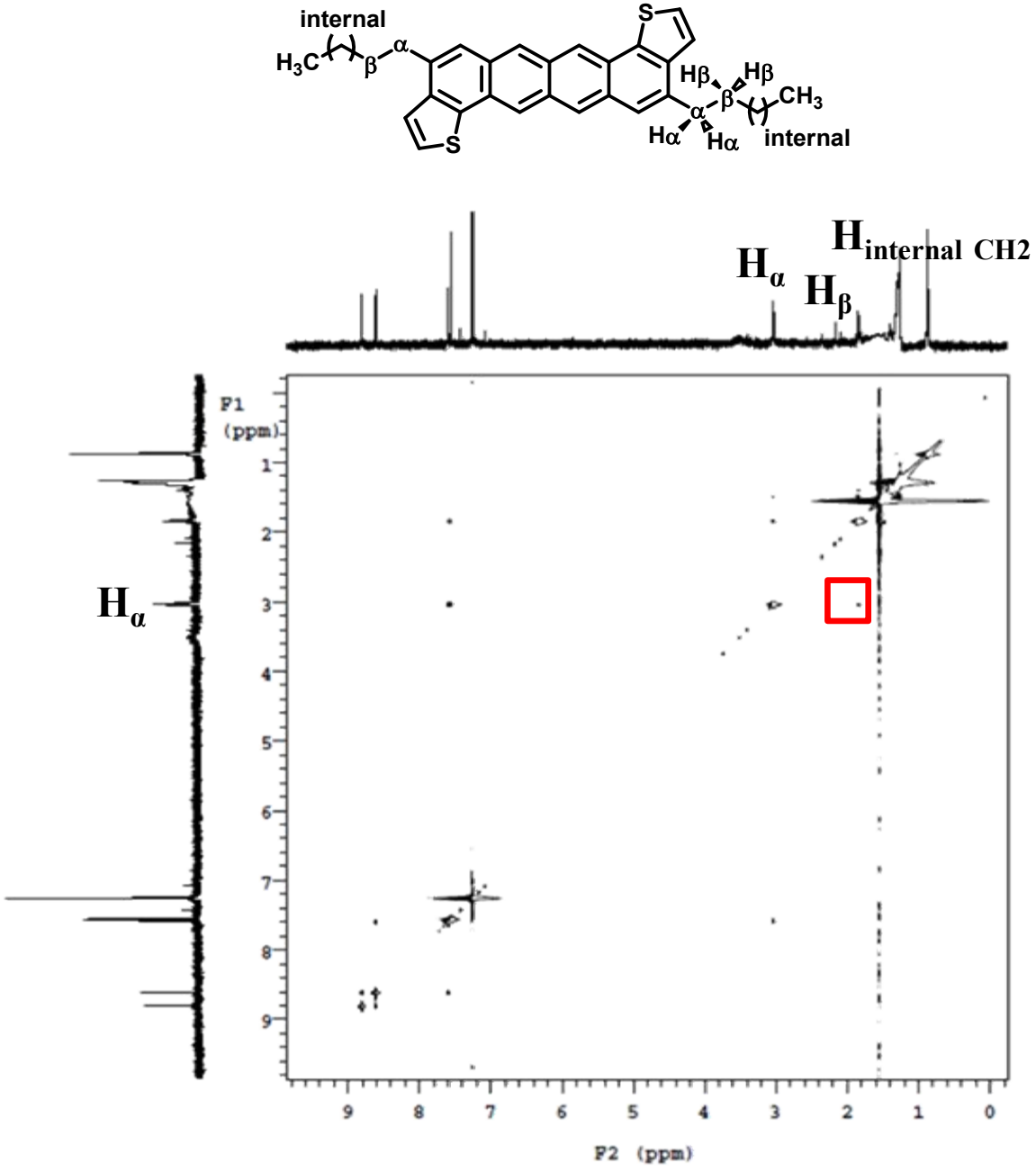



**Figure S8** ROESY spectrum of **aTDT1**. ($H_\alpha$-$H_\beta$ coupling only)

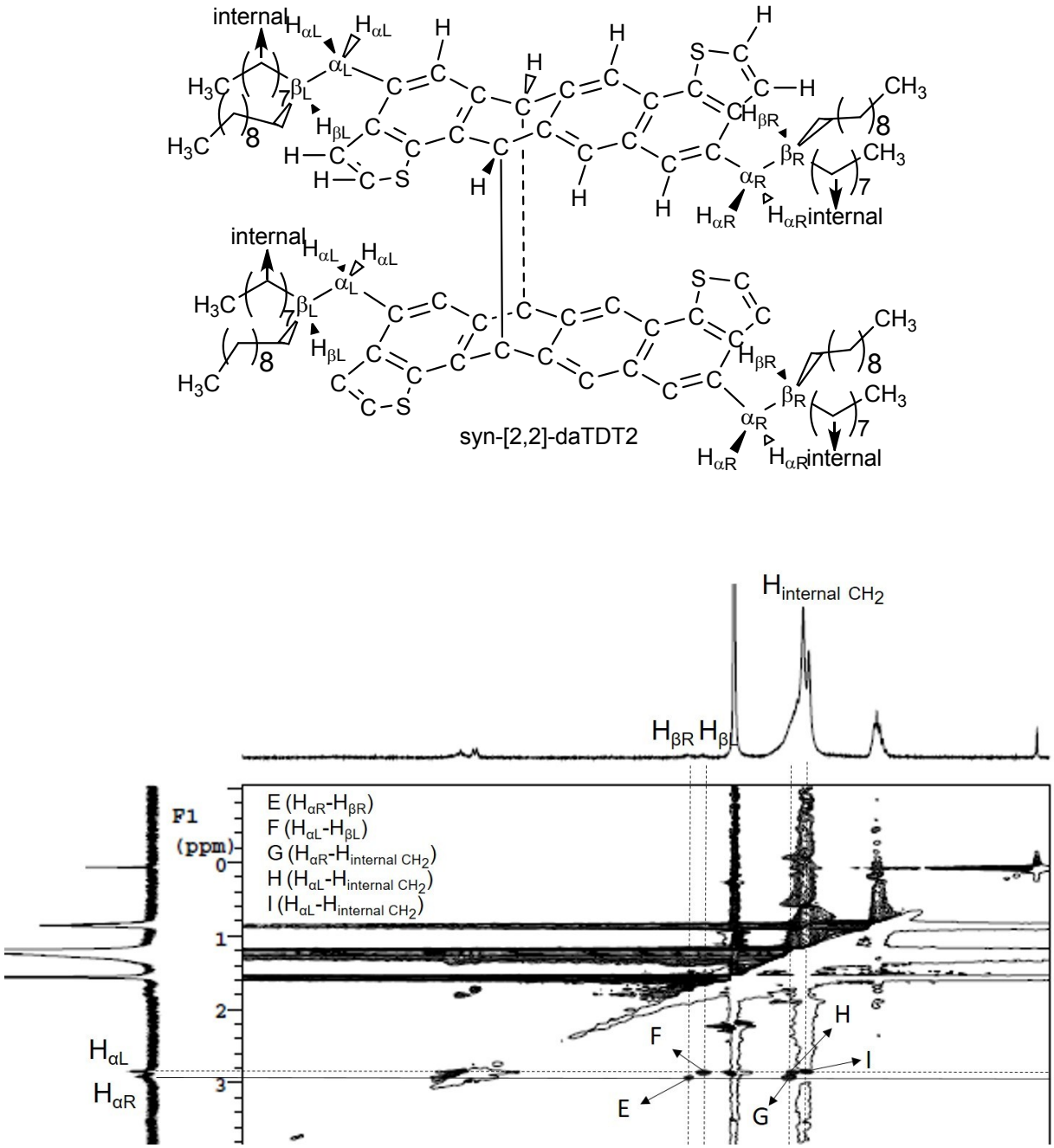



**Figure S9** Magnified ROESY spectrum of **daTDT2**.

## 5. Concentration dependent emission spectra of aTDT1

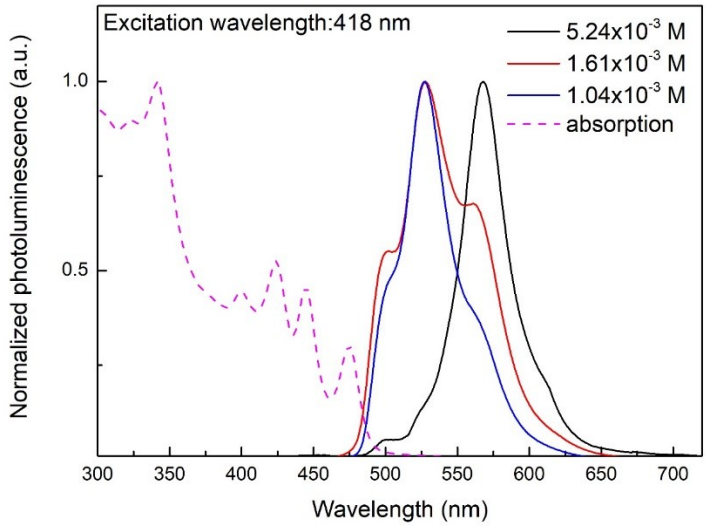



**Figure S10** Absorption spectrum (dash line) and concentration dependent emission spectra of aTDT1.

## 6. The powder x-ray diffraction (XRD) pattern of aTDT1 and the simulated pattern

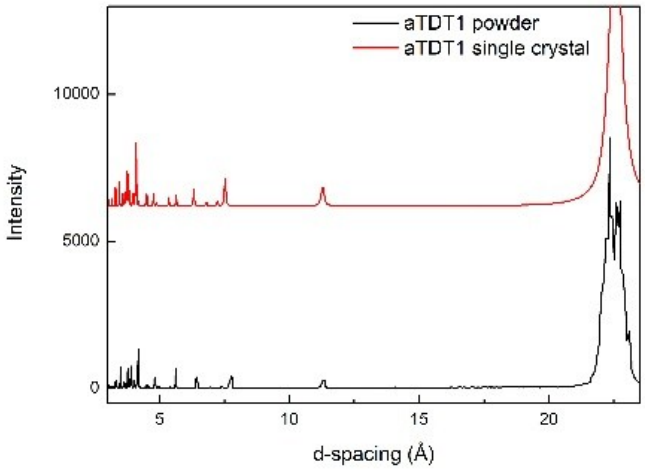



**Figure S11.** The powder x-ray diffraction (XRD) pattern of aTDT1 ( $\lambda$ = 1.320898 Å) and the simulated pattern derived from the aTDT1 single crystal structure ($\lambda$ = 1.54056 Å).

## 7. Photodimerization of aTDT2 thin film after irradiation of 15 min

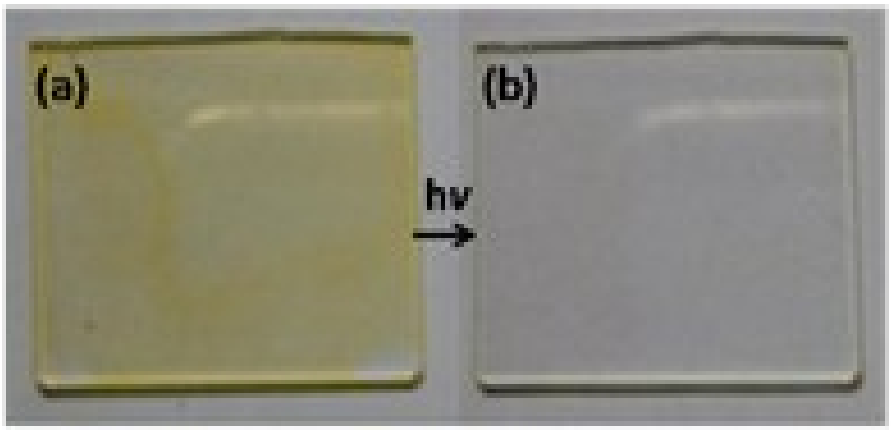



**Figure S12** Photodimerization of aTDT2 thin film, (a) before (b) after irradiation of 15 min.

## 8. X-ray diffraction (XRD) pattern of aTDT2 powder and thin film

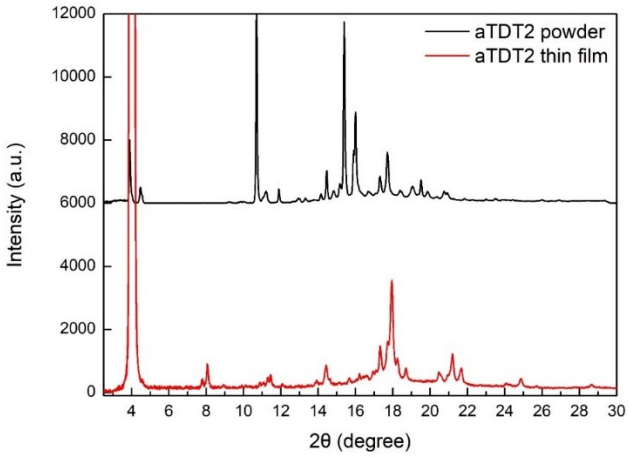



**Figure S13** The x-ray diffraction (XRD) pattern of aTDT2 powder and thin film.

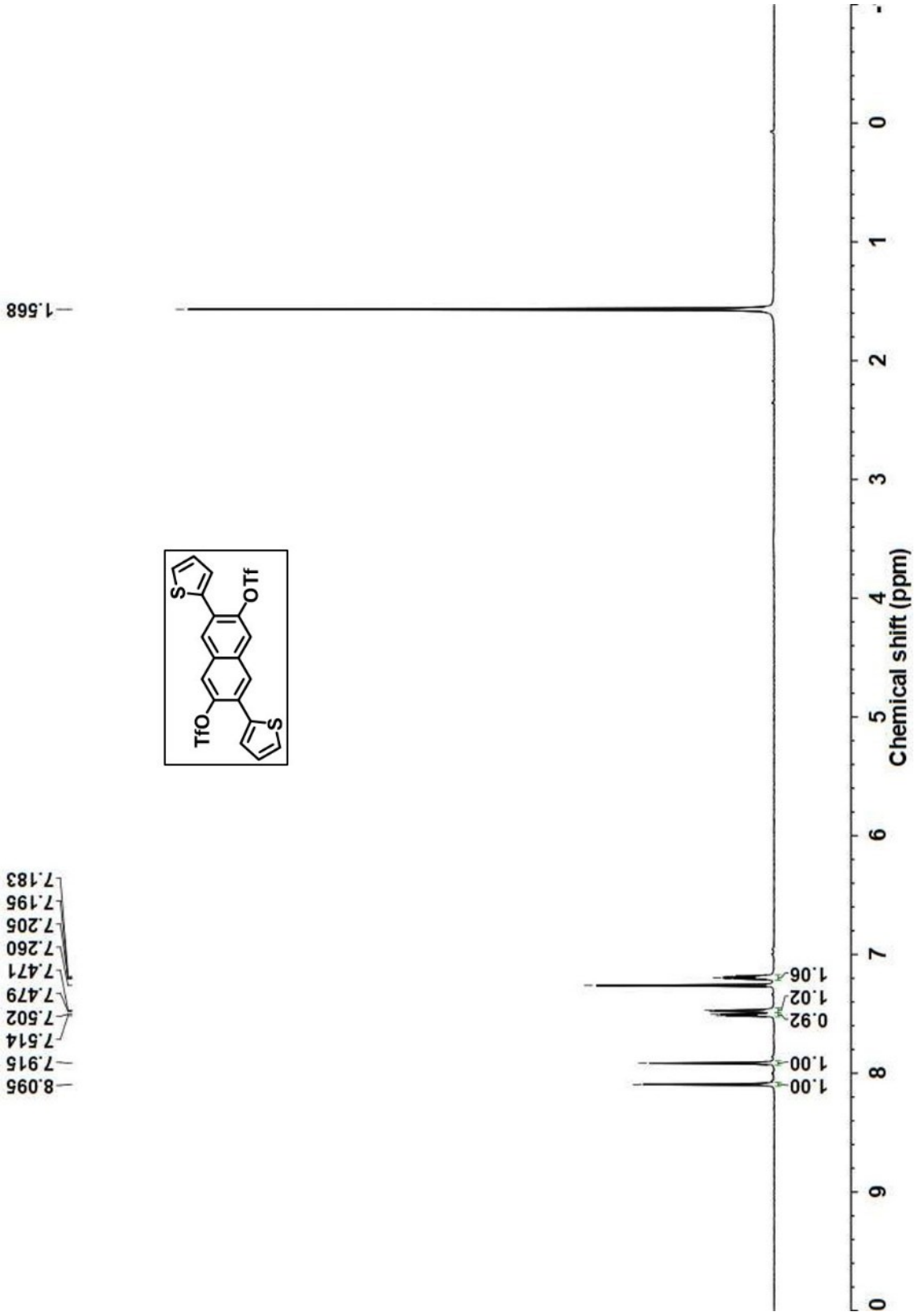
## 9. Single crystal data of aTDT1

Crystal data and structure refinement for cu_141239lt_0m_a.

| | | |
|---|---|---|
| Identification code | cu_141239lt_0m_a | |
| Empirical formula | C42 H52 S2 | |
| Formula weight | 620.95 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/c | |
| Unit cell dimensions | a = 4.8832(3) Å | α= 90°. |
| | b = 7.6289(4) Å | β= 90.819(3)°. |
| | c = 45.134(3) Å | γ = 90°. |
| Volume | 1681.21(17) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.227 $Mg/m^3$ | |
| Absorption coefficient | 1.636 $mm^{-1}$ | |
| F(000) | 672 | |
| Crystal size | 0.20 x 0.02 x 0.01 $mm^3$ | |
| Theta range for data collection | 0.979 to 66.614°. | |
| Index ranges | -5<=h<=3, -8<=k<=9, -53<=l<=50 | |
| Reflections collected | 11508 | |
| Independent reflections | 2958 [R(int) = 0.0379] | |
| Completeness to theta = 67.679° | 97.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9492 and 0.7898 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2958 / 0 / 201 | |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.100 |
| Final R indices [I>2sigma(I)] | R1 = 0.0832, wR2 = 0.2677 |
| R indices (all data) | R1 = 0.0857, wR2 = 0.2736 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.514 and -0.492 e.$Å^{-3}$ |

## 10. $^{1}H$ and $^{13}C$ NMR spectra

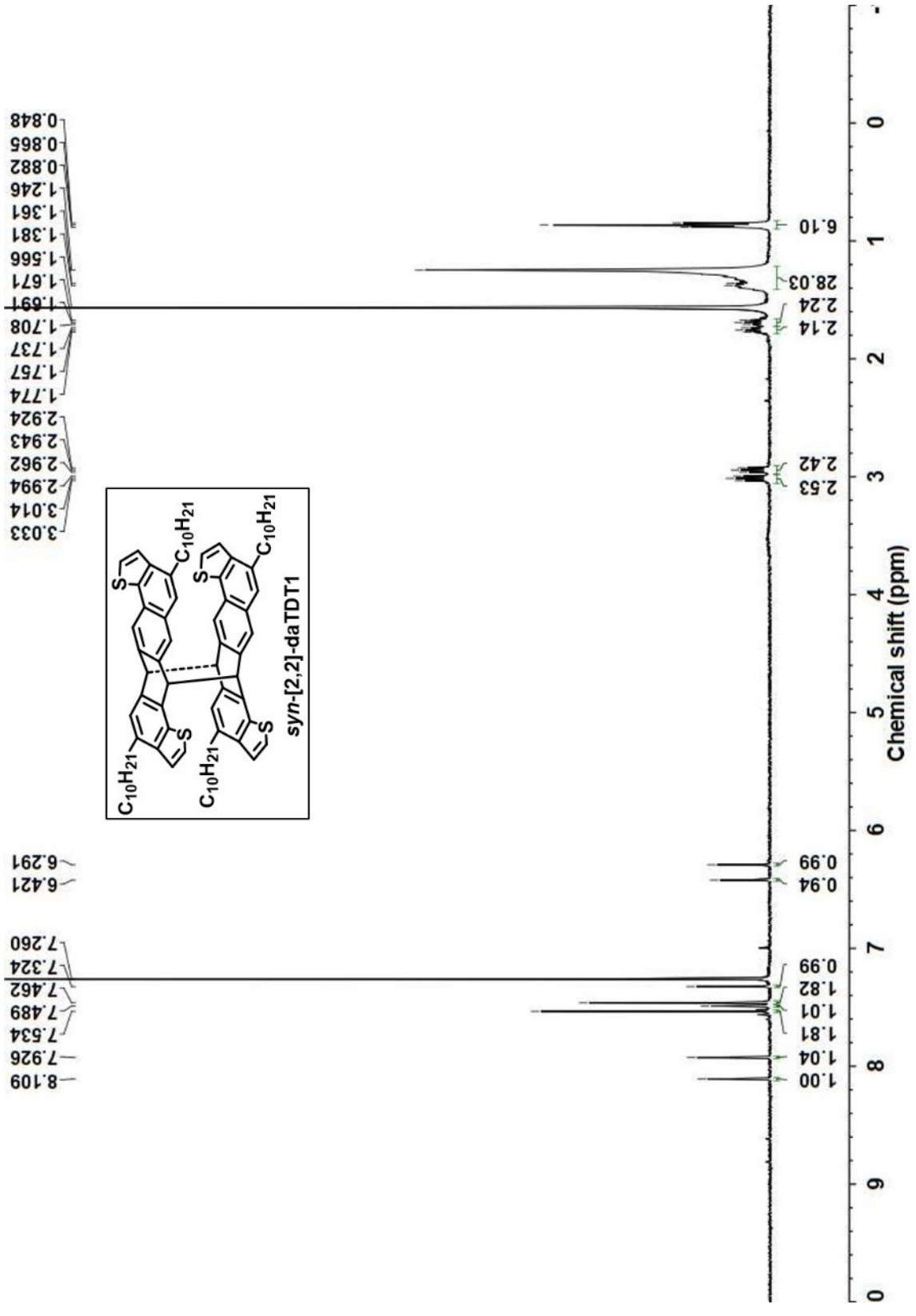


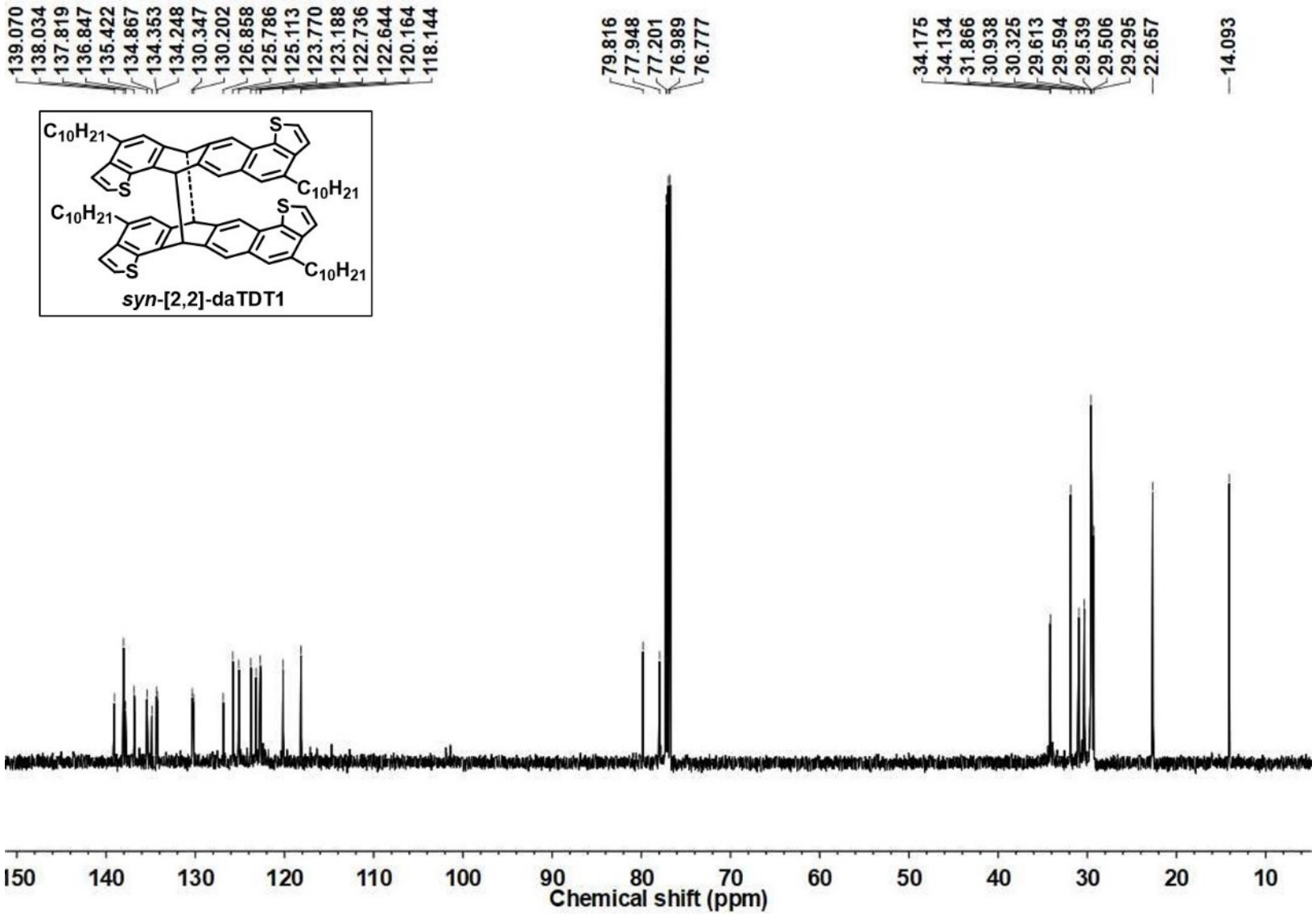
145.766
135.661
131.229
130.380
128.741
128.343
128.101
127.768
123.264
120.216
120.070
116.877
113.685
TfO
OTf
S
S
Chemical shift (ppm)
70
160
150
140
130
120
110
100
90
80
7

0.862
0.880
0.896
1.256
1.277
1.411
1.431
1.446
1.544
1.579
1.597
1.616
1.635
2.433
2.451
2.469
7.112
7.121
7.124
7.134
7.260
7.365
7.367
7.377
7.379
7.638
7.640
7.647
7.649
7.864
7.966
S
S
$C_{10}H_{21}$
$C_{10}H_{21}$
3.06
12.17
2.29
2.23
2.07
1.07
0.96
0.98
1.00
1.00
0
1
2
3
4
5
6
7
8
9
Chemical shift (ppm)

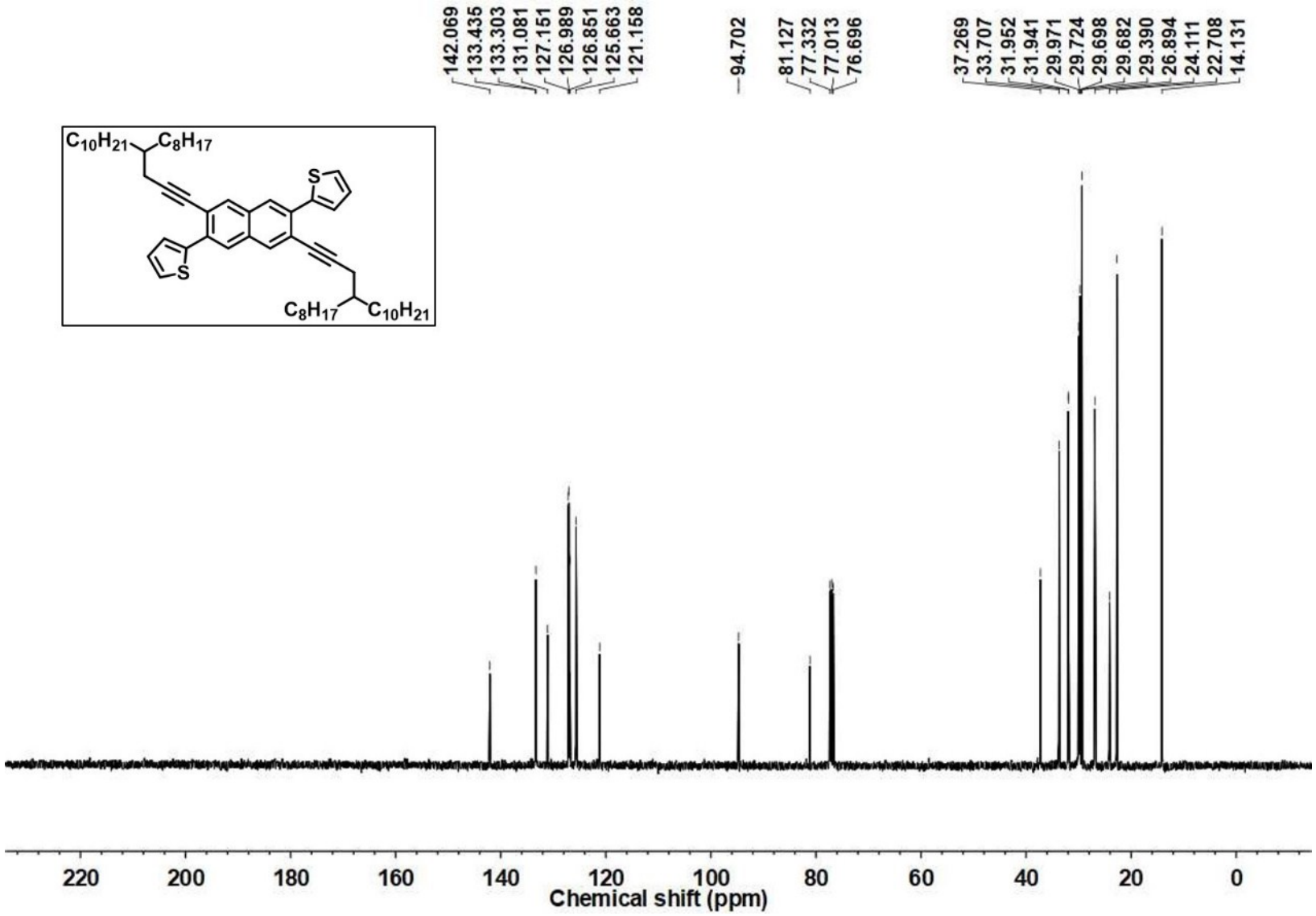
14.105
19.818
22.678
28.364
29.009
29.199
29.332
29.553
29.604
31.902
76.582
76.669
77.189
77.305
80.295
95.891
120.973
125.745
126.820
126.983
127.142
131.077
133.169
133.431
142.033
S
S
$C_{10}H_{21}$
$C_{10}H_{21}$
0
20
40
60
80
100
120
140
160
180
200
220
Chemical shift (ppm)

8.810
8.614
7.600
7.560
7.260
3.056
3.036
3.016
1.860
1.843
1.824
1.565
1.489
1.396
1.274
0.896
0.879
0.861
1.04
1.07
2.00
0.95
2.29
2.49
14.32
3.42
aTDT1
Chemical shift (ppm)


syn-[2,2]-daTDT1
Chemical shift (ppm)

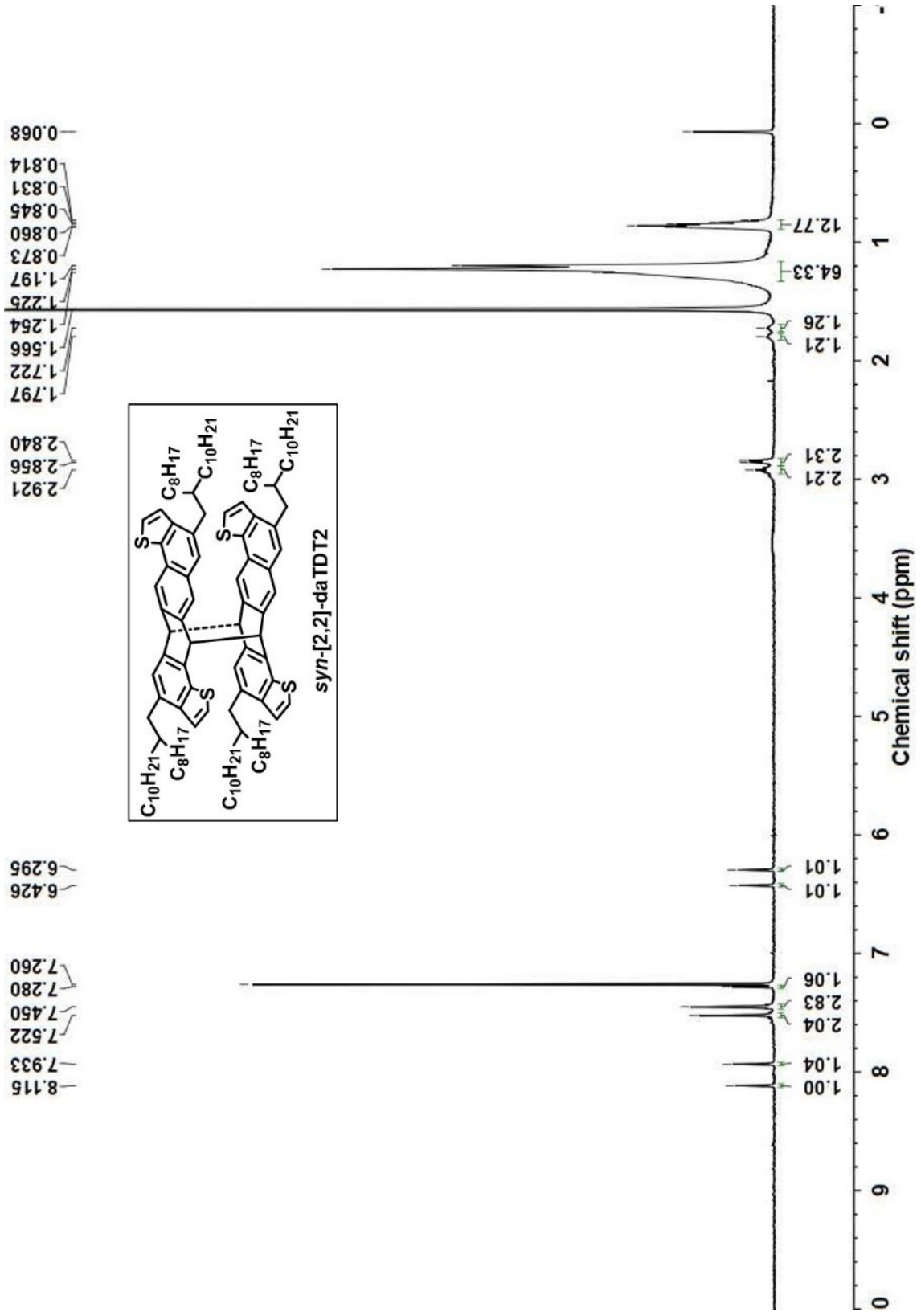

139.070
138.034
137.819
136.847
135.422
134.867
134.353
134.248
130.347
130.202
126.858
125.786
125.113
123.770
123.188
122.736
122.644
120.164
118.144
79.816
77.948
77.201
76.989
76.777
34.175
34.134
31.866
30.938
30.325
29.613
29.594
29.539
29.506
29.295
22.657
14.093
C10H21
S
C10H21
S
C10H21
S
C10H21
S
syn-[2,2]-daTDT1
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical shift (ppm)

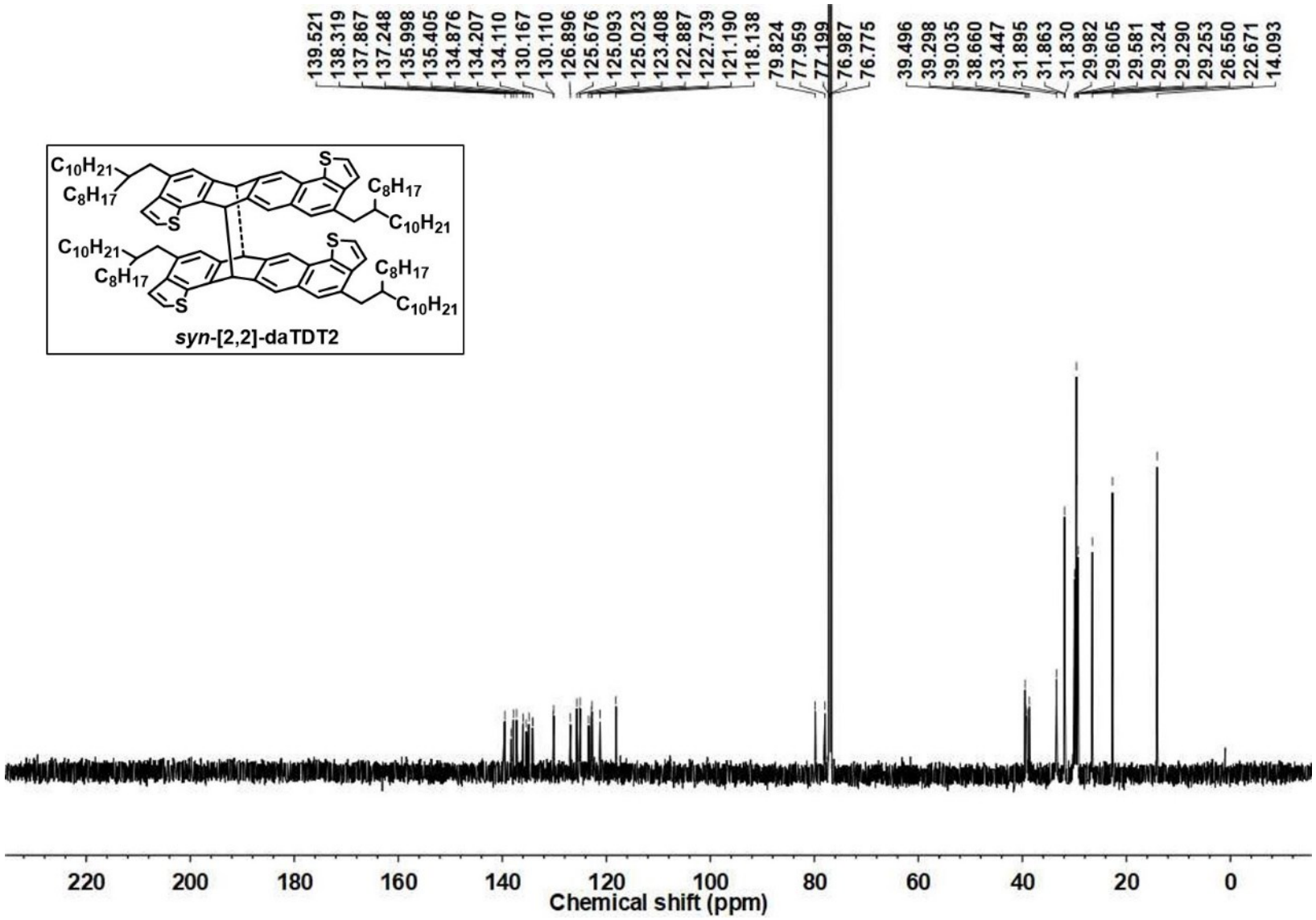
7.976
7.871
7.646
7.637
7.373
7.360
7.129
7.120
7.108
2.455
2.441
1.571
1.384
1.372
1.350
1.291
0.899
0.884
0.867
1.00
1.02
1.03
1.01
1.06
2.17
1.08
32.01
6.06
C10H21
C8H17
C8H17
C10H21
S
S
Chemical shift (ppm)


142.069
133.435
133.303
131.081
127.151
126.989
126.851
125.663
121.158
94.702
81.127
77.332
77.013
76.696
37.269
33.707
31.952
31.941
29.971
29.724
29.698
29.682
29.390
26.894
24.111
22.708
14.131
C10H21
C8H17
S
S
C8H17
C10H21
220
200
180
160
140
120
100
80
60
40
20
0
Chemical shift (ppm)

8.811
8.613
7.645
7.260
2.949
2.933
1.890
1.569
1.390
1.229
0.856
0.839
-0.001
1.00
1.05
3.02
2.00
1.22
33.21
6.52
Chemical shift (ppm)
S
S
C10H21
C8H17
C8H17
C10H21

-0.017
14.103
22.667
26.587
29.335
29.654
30.050
31.901
33.572
38.177
39.574
76.674
77.310
120.782
124.084
124.463
124.826
126.041
126.688
129.994
130.277
134.782
137.250
137.495
S
S
C10H21
C8H17
C8H17
C10H21
0
20
40
60
80
100
120
140
160
Chemical shift (ppm)


syn-[2,2]-daTDT2
Chemical shift (ppm)


139.521
138.319
137.867
137.248
135.998
135.405
134.876
134.207
134.110
130.167
130.110
126.896
125.676
125.093
125.023
123.408
122.887
122.739
121.190
118.138
79.824
77.959
77.199
76.987
76.775
39.496
39.298
39.035
38.660
33.447
31.895
31.863
31.830
29.982
29.605
29.581
29.324
29.290
29.253
26.550
22.671
14.093
C10H21
C8H17
S
C8H17
C10H21
C10H21
C8H17
S
C8H17
C10H21
syn-[2,2]-daTDT2
220
200
180
160
140
120
100
80
60
40
20
0
Chemical shift (ppm)

## 11. Reference

1. S. Shinamura, I. Osaka, E. Miyazaki, A. Nakao, M. Yamagishi, J. Takeya, K. Takimiya, *J. Am. Chem. Soc.* **2011**, *133*, 5024.