Supramolecular chirality of coordination polymers of Ag^+ with a chiral thiol ligand that bears a β-turn structure

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Electronic Supplementary Information (ESI)

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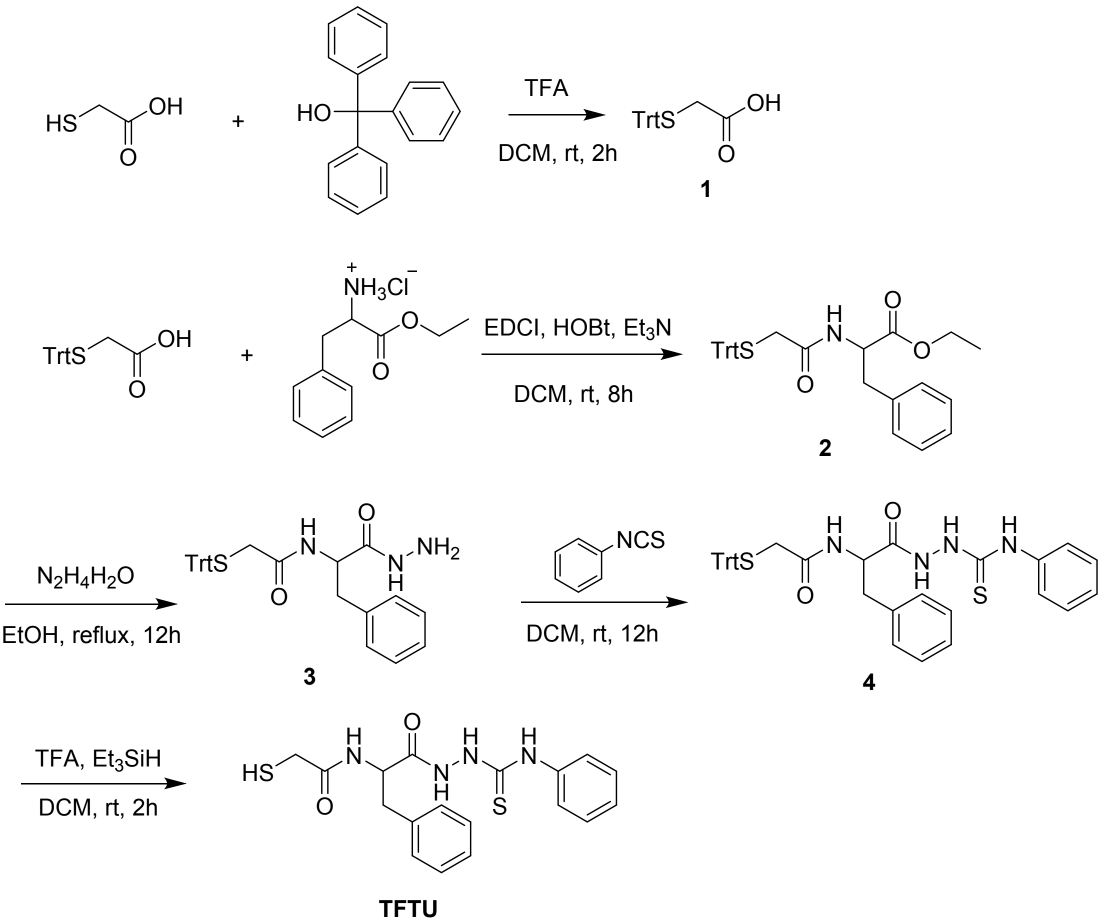
1. Syntheses and characterization



Scheme S1. General procedures for the syntheses of L-/D-**TFTU**

1: To a solution of mercaptoacetic acid (0.92 mL, 10.0 mmol) and triphenylmethanol (2.6 g, 20.0 mmol) in DCM (15 mL), TFA (15 mL) was added dropwise. The mixture was stirred for 2h at room temperature, evaporated in vacuo, and the solid residue was redissolved in DCM to purified by silica gel chromatography using DCM:MeOH = 50:1 as a mobile phase. **1** was obtained as white solid (2.2 g, 65.8 %)

2: To a solution of **1** (0.67 g, 2.0 mmol) and Et_3N (0.5 mL) in DCM (10 mL) was added EDCI (0.58 g, 3.0 mmol) and HOBT (0.40 g, 3.0 mmol) at 0℃. After 30 min, a solution of (L or D) **Phe-OEt-HCl** (0.58 g, 2.5 mmol) and Et_3N (0.5 mL) in DCM (10 mL) was added. The mixture was left to stand at room temperature for 8 hours, evaporated in vacuo, and the solid residue was dissolved in AcOEt. The solution was washed successively with 1% $NH_3 \cdot H_2O$, dilute HCl, pure water and saturate NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, then purified by flash chromatography on silica gel using DCM as a mobile phase, affording a white powder (0.70 g, 68.8 %).

3: Excess aqueous hydrazine (80%) was added to **2** which was dissolved in ethanol (10 mL) and refluxed overnight, evaporated in vacuo. The oily solid was dissolved in DCM and purified by flash chromatography on silica gel using DCM:MeOH =50:1 as a mobile phase, affording a white solid (0.53 g, 77.5 %).

4: To a solution of **3** (0.50 g, 1.0 mmol) in CH_2Cl_2 (10 mL), 0.5 mL **Phe-NCS** was added dropwise. The mixture was stirred at room temperature overnight and filtered the solid, which after washing by DCM gave **4** as white solid (0.29 g, 74.7 %).

TFTU: **4** (0.063 g, 0.1 mmol) was dissolved in 10 mL DCM, 0.3 mL TFA and 0.03 mL Et_3SiH was added dropwise. The mixture was left to stir at room temperature for 2h and concentrated under reduced pressure. The residue was washed with PE thrice and then dried to give **TFTU** as white solid (0.032 g, 82.5 %).

L-**TFTU**:

^{1}H NMR (500 MHz, DMSO-*d*$_6$): *δ* (ppm) 10.34 (s, 1H), 9.74 (s, 1H), 9.18 (s, 1H), 8.47 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 4.4 Hz, 4H), 7.20 (td, *J* = 8.5, 4.1 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 4.44 (s, 1H), 3.12 (dd, *J* = 22.0, 7.6 Hz, 3H), 2.88 (dd, *J* = 12.7, 9.4 Hz, 1H), 2.59 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, CD_3CN): *δ* (ppm) 181.92, 171.42, 170.50, 138.67, 136.62, 129.39, 128.60, 128.38, 126.95, 125.77, 124.99, 54.96, 36.16, 27.41.

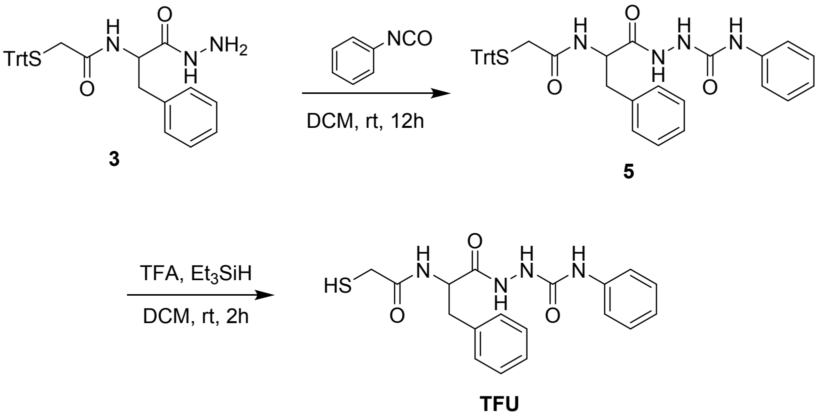
HRMS (ESI): calcd for $[C_{18}H_{20}N_4NaO_2S_2]^+$: 411.0920, found: 411.0923.

D-**TFTU**:

^{1}H NMR (500 MHz, DMSO-*d*$_6$): *δ* (ppm) δ 10.34 (s, 1H), 9.74 (s, 1H), 9.18 (s, 1H), 8.47 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 4.4 Hz, 4H), 7.20 (td, *J* = 8.5, 4.1 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 4.44 (s, 1H), 3.12 (dd, *J* = 22.0, 7.6 Hz, 3H), 2.88 (dd, *J* = 12.7, 9.4 Hz, 1H), 2.59 (t, *J* =7.9 Hz, 1H).

^{13}C NMR (101 MHz, CD_3CN): *δ* (ppm) 181.94, 171.42, 170.46, 138.60, 136.62, 129.39, 128.60, 128.38, 126.95, 125.76, 124.98, 54.97, 36.11, 27.40.

HRMS (ESI): calcd for $[C_{18}H_{20}N_4NaO_2S_2]^+$: 411.0920, found: 411.0922.



Scheme S2. General procedures for the syntheses of **TFU**

5: To a solution of **3** (0.26 g, 0.5 mmol) in CH_2Cl_2 (10 mL), 0.3 mL **Phe-NCO** was added dropwise. The mixture was stirred at room temperature overnight and filtered the solid, which after washing by DCM gave **5** as white solid (0.28 g, 91.1 %).

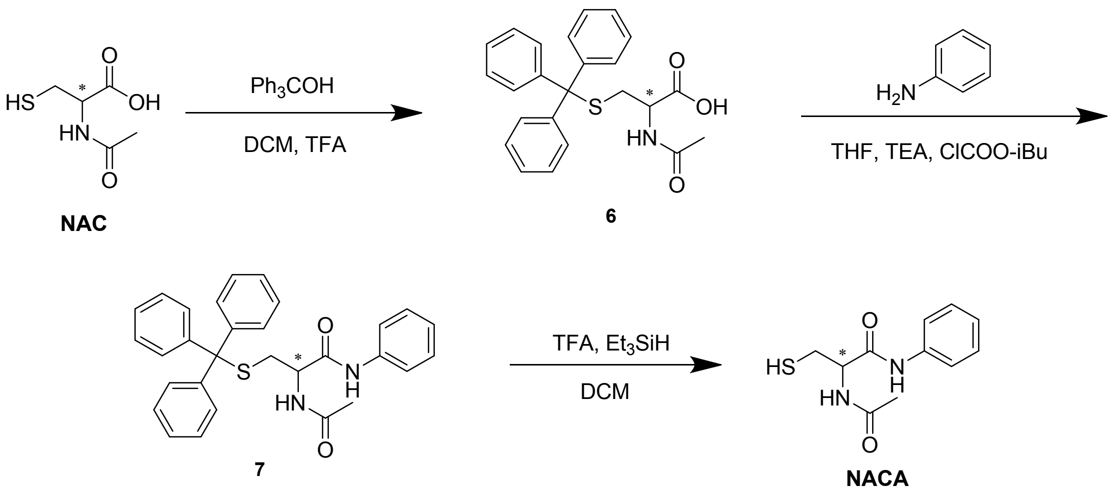
TFU: **5** (0.061 g, 0.1 mmol) was dissolved in 10 mL DCM, 0.3 mL TFA and 0.03 mL Et_3SiH was added dropwise. The mixture was left to stir at room temperature for 2h and concentrated under reduced pressure. The residue was washed with PE thrice and then dried to give **TFU** as white solid (0.027 g, 72.5 %).

L-**TFU**:

^1H NMR (500 MHz, DMSO-*d*$_6$):δ (ppm) 10.03 (s, 1H), 8.54 (s, 1H), 8.41 (d, J = 6.9 Hz, 1H), 8.16 (s, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 4.4 Hz, 3H), 7.24 (d, J = 8.0 Hz, 2H), 7.21 (dt, J = 8.6, 4.1 Hz, 1H), 6.95 (t, J = 7.3 Hz, 1H), 4.49 (s, 1H), 3.13 (d, J = 7.9 Hz, 2H), 3.06 (dd, J = 13.9, 4.8 Hz, 1H), 2.84 (dd, J = 13.7, 9.4 Hz, 1H), 2.58 (t, J = 7.9 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ (ppm) 171.42, 170.38, 155.65, 140.02, 137.82, 129.71, 129.12, 128.63, 126.89, 122.39, 118.84, 53.66, 37.75, 27.41.

HRMS (ESI): calcd for $[C_{18}H_{21}N_4O_3S]^+$: 373.1329, found: 373.1331.



Scheme S3. General procedures for the syntheses of **NACA**

6: To a solution of N-Acetyl-L/D-cysteine (1.63 g, 10.0 mmol) and triphenylmethanol (2.5 g, 20.0 mmol) in DCM (20 mL), TFA (5 mL) was added dropwise. The mixture was stirred for 3h at room temperature, evaporated in vacuo, and the solid residue was redissolved in DCM to purified by silica gel chromatography using DCM:MeOH = 100:1 as a mobile phase. **6** was obtained as white solid (3.22 g, 79.5 %)

7: To a solution of **6** (0.61 g, 1.5 mmol) and Et$_3$N (0.21 mL) in THF (20 mL), isobutyl choroformate (0.20 g) was added at 0 ºC. The mixture was stirred for 1 h at 0 ºC, then aniline (0.15 g, 1.6 mmol) was added, and the solution was stirred under N$_2$ atmosphere at room temperature overnight. The mixture was quenched by water and poured in 30 mL EA, washed by saturated NaHCO$_3$, 1% dilute HCl and saturated NaCl successively. The organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure, then purified by flash chromatography on silica gel using DCM:MeOH = 250:1 as a mobile phase. **7** was obtained as yellow solid (0.336 g, 47 %)

NACA: **7** was dissolved in 15 mL DCM, 3.3 mL TFA and 0.33 mL Et$_3$SiH was added dropwise. The mixture was left to stir at room temperature for 3h and concentrated under reduced pressure. The residue was purified by silica gel chromatography using DCM:MeOH = 100:1 as a mobile phase to give **NACA** as white solid (0.08 g, 48 %)

L-**NACA**:

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 10.10 (s, 1H), 8.24 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 4.52 (dd, J = 13.8, 7.7 Hz, 1H), 2.89 – 2.79 (m, 1H), 2.73 (dt, J = 13.4, 7.7 Hz, 1H), 2.35 (t, J = 8.3 Hz, 1H), 1.89 (s, 3H).

^{13}C NMR (214 MHz, DMSO-d_6): δ (ppm) 169.50, 168.86, 138.73, 128.70, 123.50, 119.38, 55.94, 25.95, 22.47.

HRMS (ESI): calcd for $[C_{11}H_{14}N_2NaO_2S]^+$: 261.0668, found:261.0670.

D-**NACA**:

^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 10.10 (s, 1H), 8.24 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 4.52 (dt, J = 13.8, 7.0 Hz, 1H), 2.89 – 2.80 (m, 1H), 2.73 (dt, J = 13.4, 7.8 Hz, 1H), 2.37 – 2.32 (m, 1H), 1.93 (s, 3H).

^{13}C NMR (214 MHz, DMSO-d_6): δ (ppm) 169.49, 168.86, 138.73, 128.70, 123.50, 119.38, 55.94, 25.95, 22.47.

HRMS (ESI): calcd for $[C_{11}H_{14}N_2NaO_2S]^+$: 261.0668, found:261.0668..

2. Supplementary spectral data

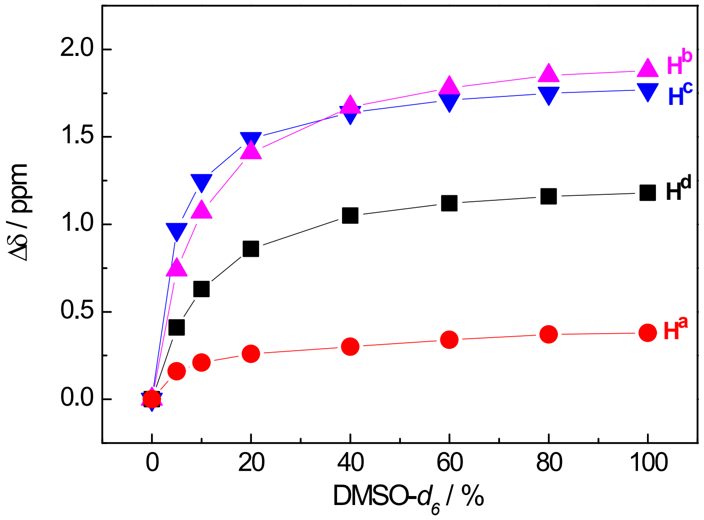


Fig. S1 Influence on -NH protons' resonances of L-**TFTU** in CD_3CN/DMSO-d_6 by volume fraction of the hydrogen bonding component DMSO-d_6. [L-**TFTU**] = 1 mM.

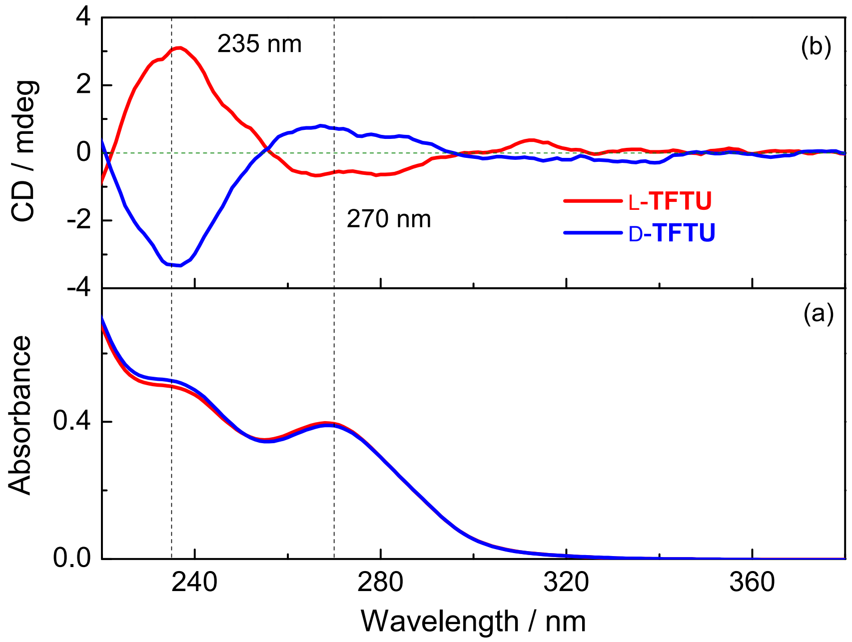


Fig. S2 Absorption (a) and CD (b) spectra of **TFTU** in CH$_3$CN. [L-**TFTU**] = [D-**TFTU**] = 40 μM.

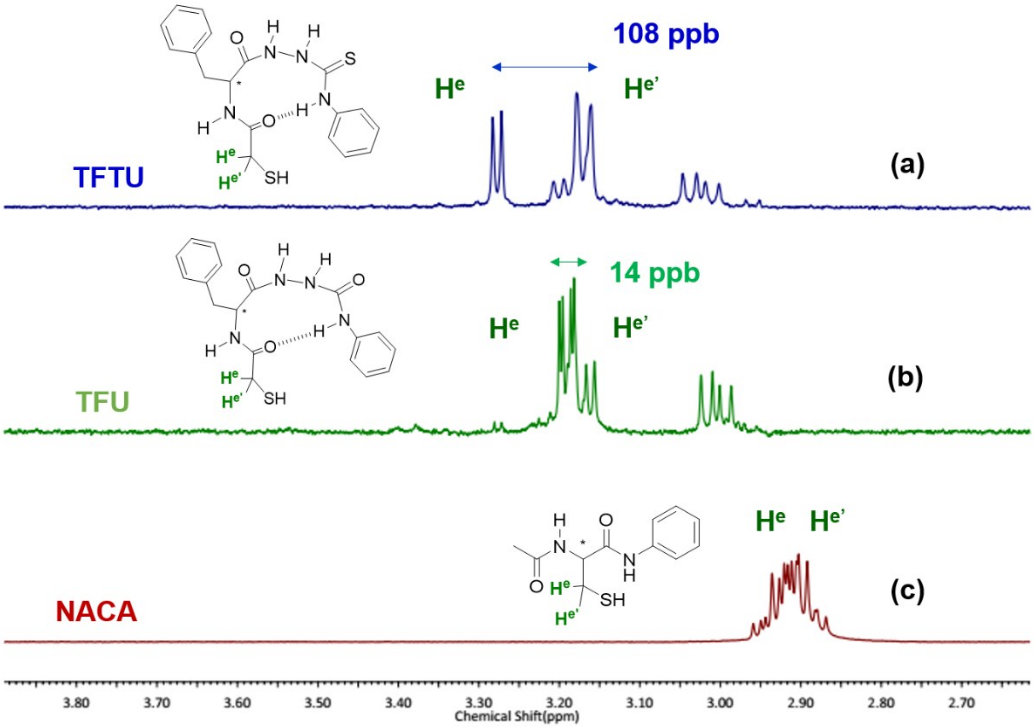


Fig. S3 Resonances of -CH$_2$- protons H^e/H$^{e'}$ of (a) L-**TFTU**, (b) L-**TFU** and (c) L-**NACA** in CD$_3$CN.

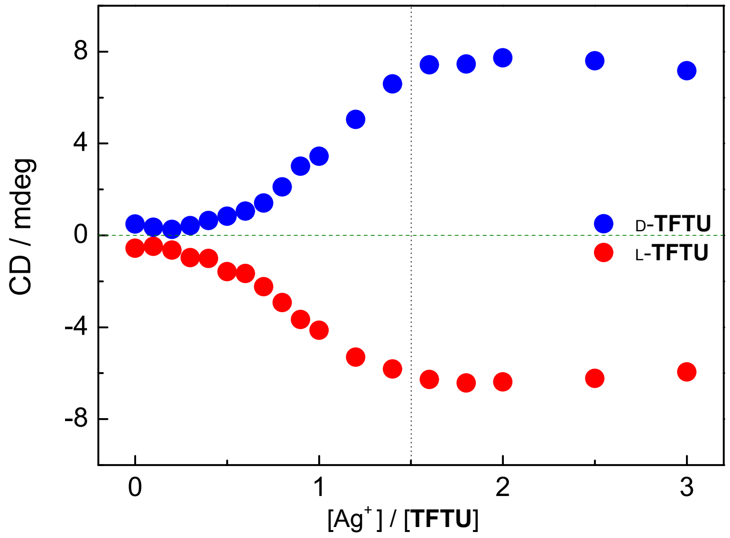


Fig. S4 Plots of CD signal of L-**TFTU** and D-**TFTU** at 275 nm versus concentration of Ag$^+$ from 0 to 3 equivalents in CH$_3$CN. [L-**TFTU**] = [D-**TFTU**] = 40 μM, [AgNO$_3$] = 0 - 120 μM.

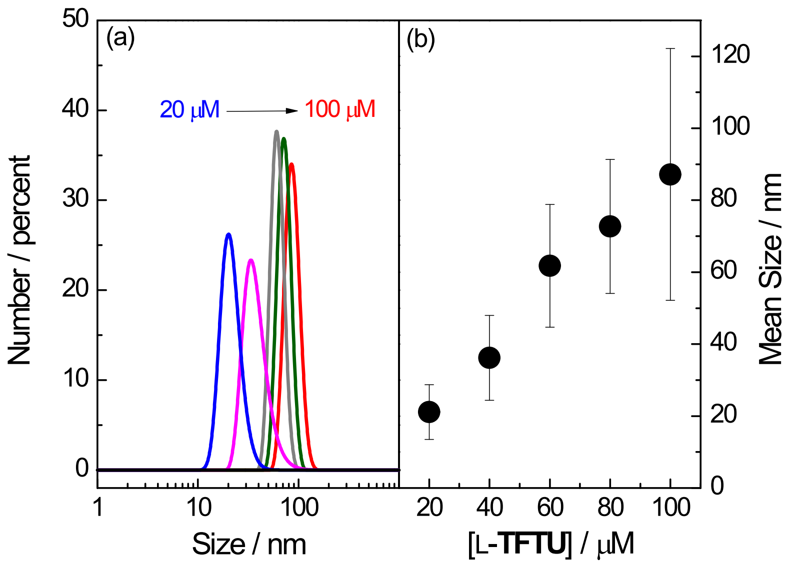


Fig. S5 DLS profiles in CH$_3$CN of L-**TFTU** of different concentration in the presence of 1.5 equivalents AgNO$_3$ (a) and mean size as a function of concentration of L-**TFTU** (b). The bar indicates the range of size distribution. [L-**TFTU**] = 20 - 100 μM.

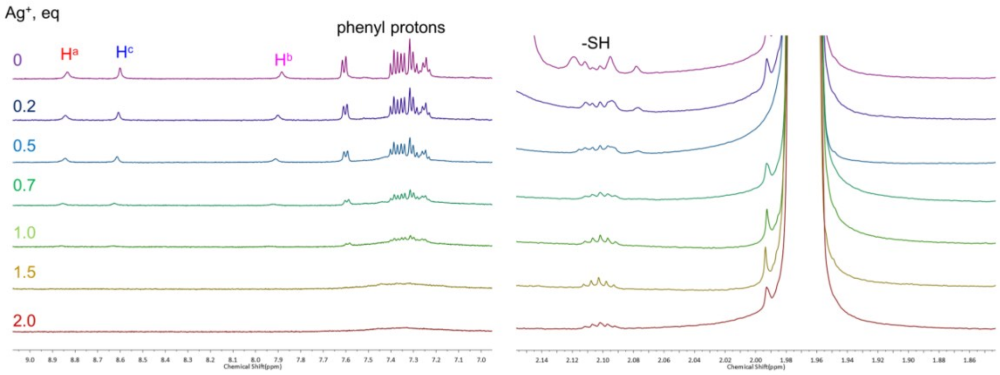


Fig. S6 Portions of ^{1}H NMR spectra of L-**TFTU** in CD_3CN in the presence of Ag^+ of increasing concentration from 0 to 2 equivalents. [L-**TFTU**] = 1 mM.

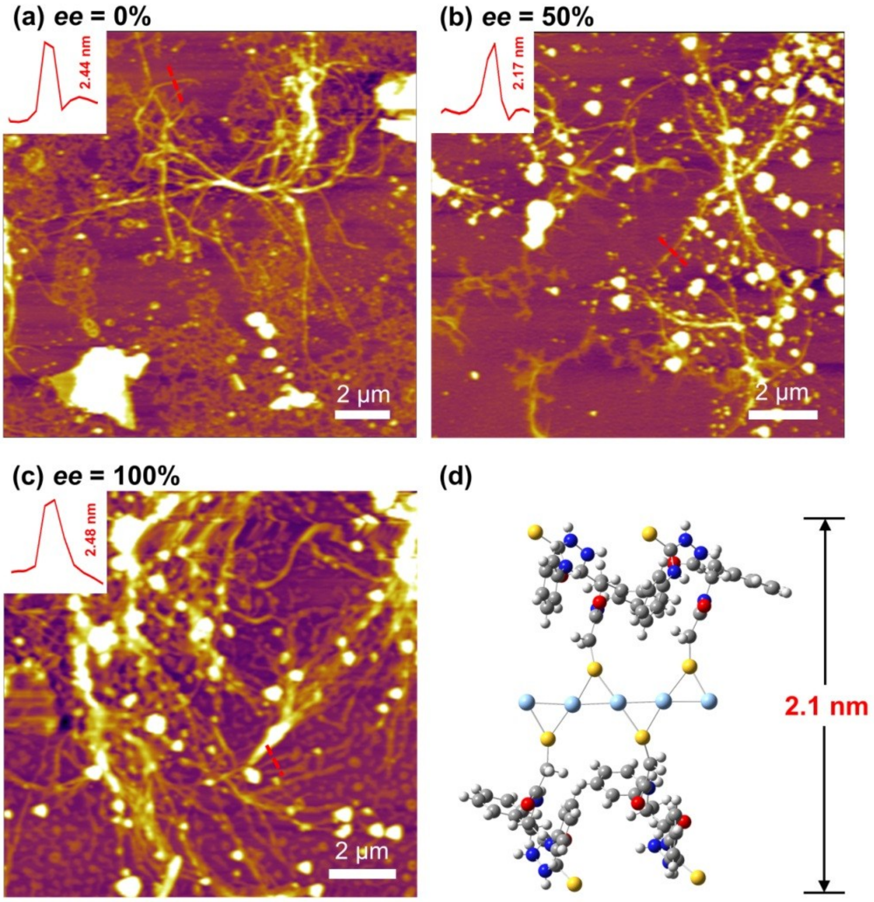


Fig. S7 AFM height images and height profiles along the red dashed line of the Ag^+-**TFTU** coordination polymers of **TFTU** *ee* 0% (a), 50% (b), and 100% (c) at the silicon wafer interface. (d) Calculated height of Ag^+-**TFTU** coordination polymers based on the structural model shown in Scheme 1b using Gaussian modeling.

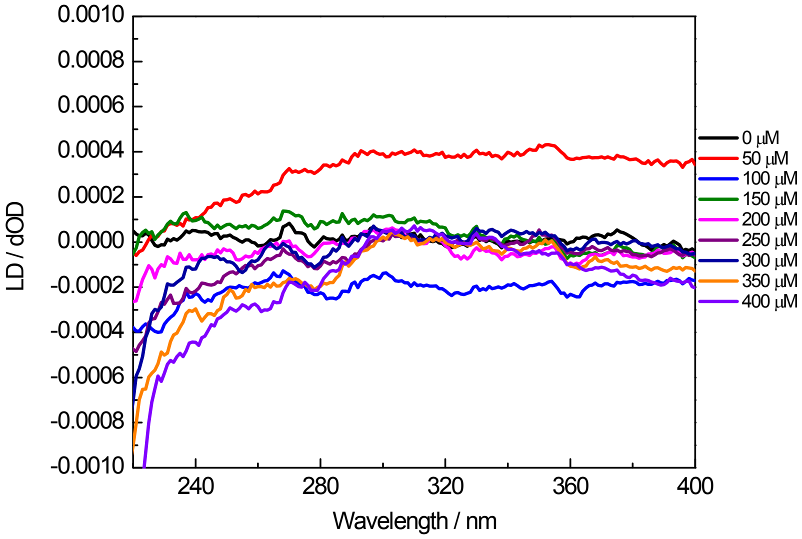


Fig. S8 LD spectra in CH_3CN of L-**TFTU** of different concentration in the presence of 1.5 equivalents $AgNO_3$. [L-**TFTU**] = 0 - 400 μM.

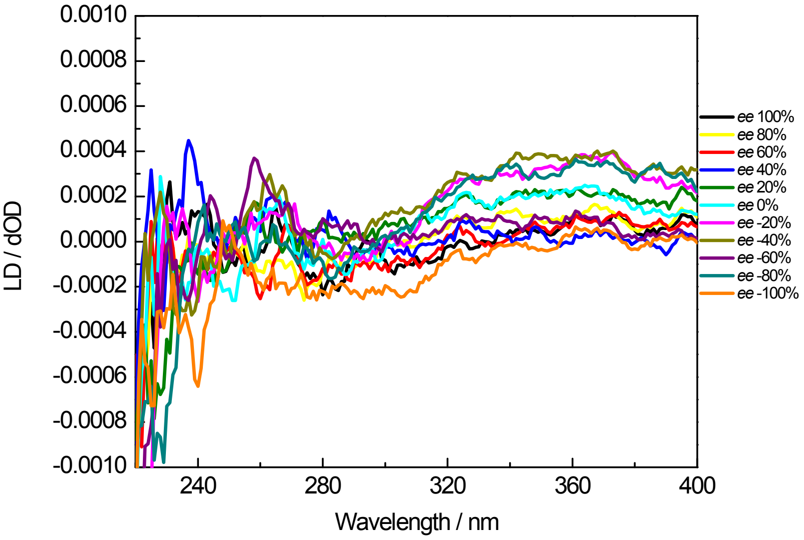


Fig. S9 LD spectra in CH_3CN of **TFTU** of varying *ee* in the presence of 1.5 equivalents $AgNO_3$. [**TFTU**] = 100 μM. [$AgNO_3$] = 150 μM.

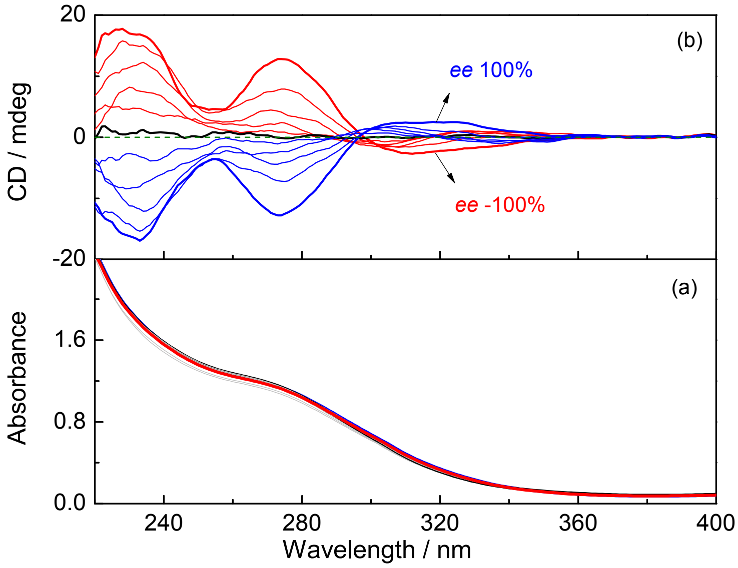


Fig. S10 Absorption (a) and CD (b) spectra in CH_3CN of **TFTU** of varying *ee* in the presence of 1.5 equivalents $AgNO_3$. [**TFTU**] = 100 μM. [$AgNO_3$] = 150 μM.

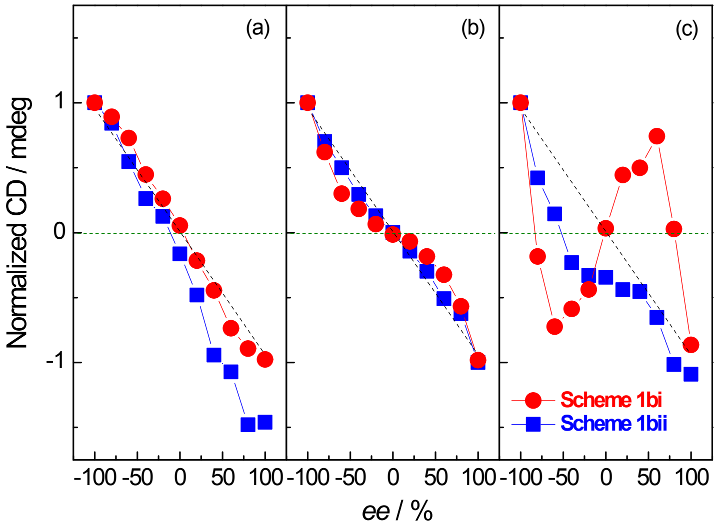


Fig. S11 CD-*ee* dependences of Ag^+-**TFTU** coordination polymers prepared from Ag^+ with chiral ligand of varying *ee* (red circle, Scheme 1bi) and from mixing immediately of the two coordination polymers respectively prepared from Ag^+ with each enantiopure ligand (blue square, Scheme 1bii), generated from CD signals at 235 nm (a), 275 nm (b) and 340 nm (c). [**TFTU**] = 100 μM. [$AgNO_3$] = 150 μM.

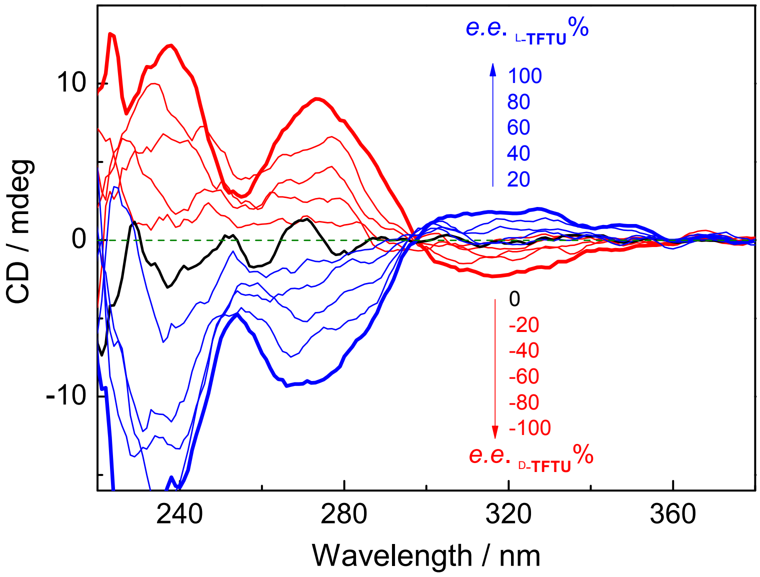


Fig. S12 CD spectra of Ag^+-**TFTU** coordination polymers measured immediately after mixing two polymers prepared respectively from each pure enantiomeric ligand with Ag^+ in CH_3CN. [**TFTU**] = 100 μM. [$AgNO_3$] = 150 μM.

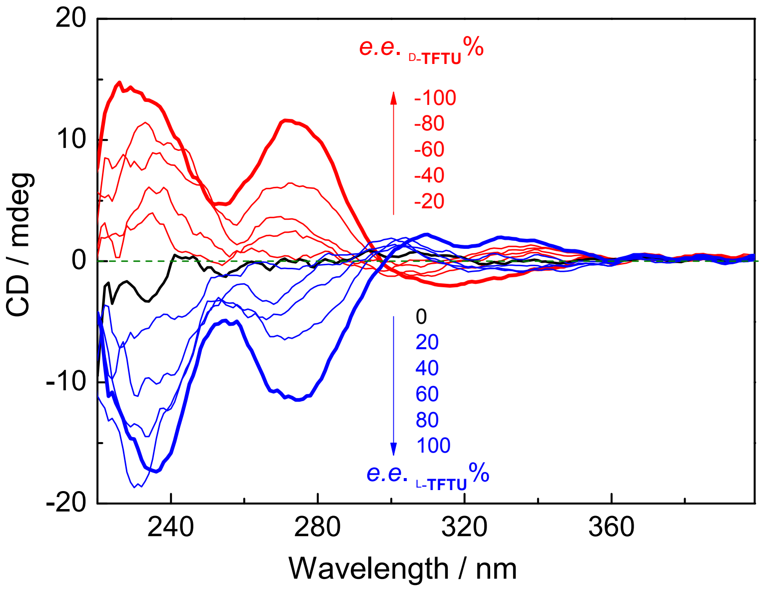


Fig. S13 CD spectra of Ag^+-**TFTU** coordination polymers 1 hour after mixing of the two polymers prepared respectively from each pure enantiomeric ligand with Ag^+ in CH_3CN. [**TFTU**] = 100 μM. [$AgNO_3$] = 150 μM.

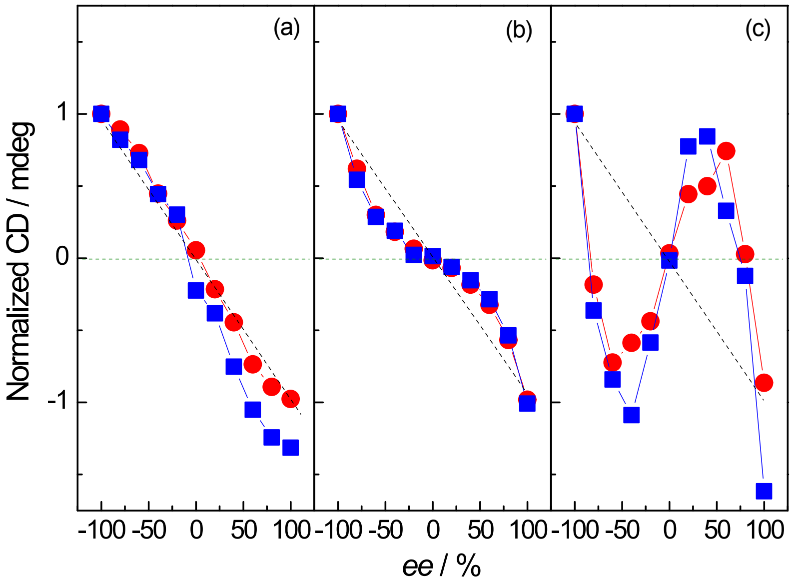


Fig. S14 CD-*ee* dependences of Ag$^+$-**TFTU** coordination polymers prepared from Ag$^+$ with chiral ligand of varying *ee* (red cirlce) and from mixing for 1 hour the two coordination polymers respectively prepared from Ag$^+$ with each enantiopure ligand (blue square), generated from CD signals at 235 nm (a), 275nm (b) and 340 nm (c). [**TFTU**] = 100 μM. [$AgNO_3$] = 150 μM.

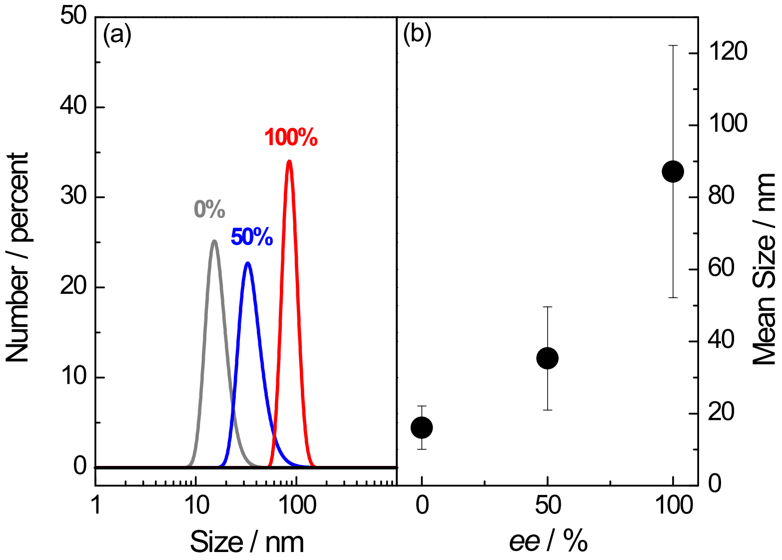


Fig. S15 DLS profiles in CH_3CN of **TFTU** of varying *ee* in the presence of 1.5 equivalents of $AgNO_3$ (a) and mean size as a function of *ee* (b). The bar indicates the range of size distribution. [**TFTU**] = 100 μM.

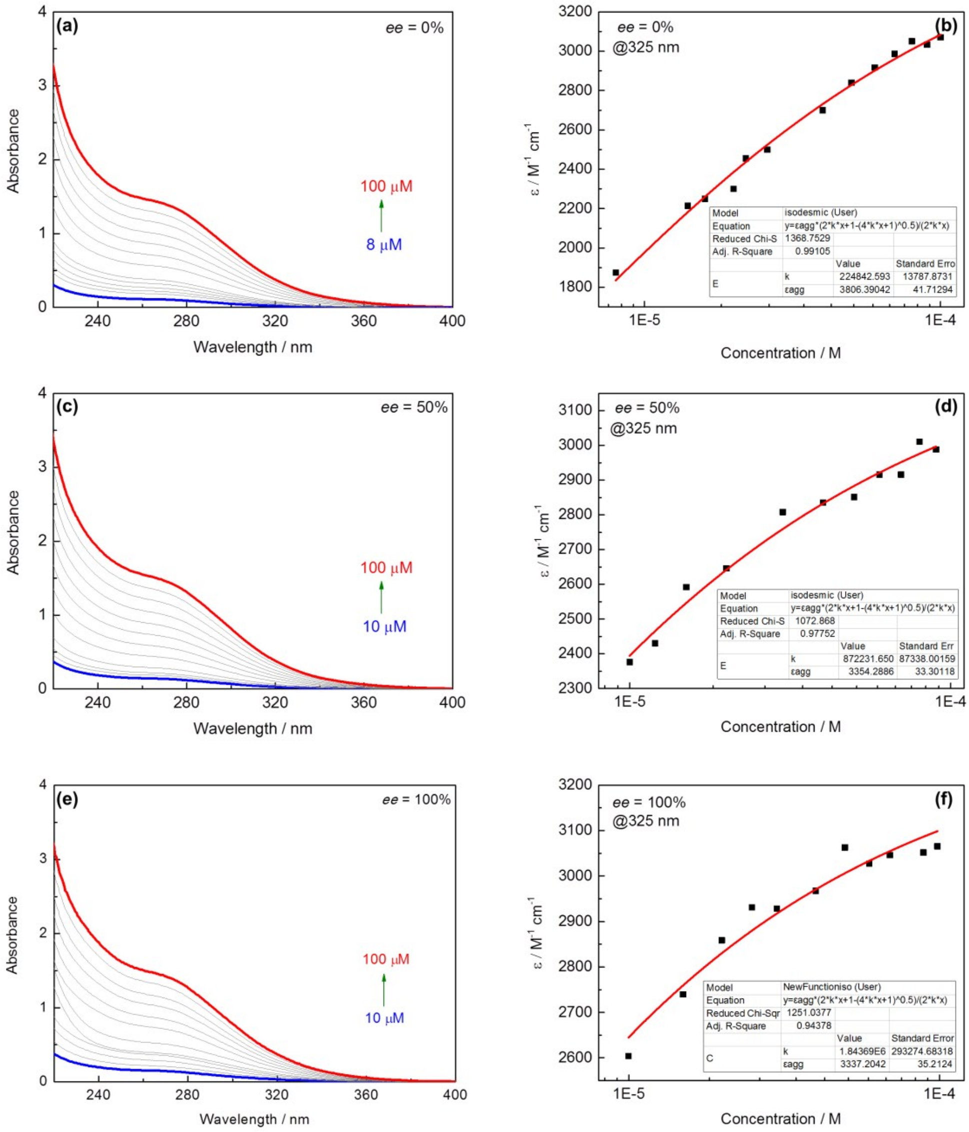


Fig. S16 Concentration-dependent absorption spectra in CH_3CN of **TFTU** of varying *ee* in the presence of 1.5 equivalents of $AgNO_3$ (a, c, e) and fitted association constants according to the isodesmic model (b, d, f).

The nonlinear curve fitting is based on concentration-dependent isodesmic self-assembly model:

$\varepsilon = \varepsilon_{\mathrm{mon}}\alpha_{\mathrm{mon}} + \varepsilon_{\mathrm{agg}}\alpha_{\mathrm{agg}}$

ε is the extinction coefficient, $\varepsilon_{\mathrm{mon}}$ is the extinction coefficient of monomer species, $\varepsilon_{\mathrm{agg}}$ is the extinction coefficient of aggregated molecules. α_{mon} is the molar fraction of monomer species, α_{agg} is the fraction of aggregated molecules. Since absorbance at 325 nm of coordination polymers relates to $Ag^+ \cdots Ag^+$ interactions, $\varepsilon_{\mathrm{mon}} = 0$.

Therefore $\varepsilon = \varepsilon_{\mathrm{agg}}\alpha_{\mathrm{agg}}$ at 325 nm.

The isodesmic (equal *K*) aggregation process: $K = K_2 = K_3 = \cdots = K_n$

The concentration of *n*-mer c_n and the total concentration of molecules *c*, respectively, can be given as (see Reference: Z. Chen, A. Lohr, C. R. Saha-Möller and F. Würthner, *Chem. Soc. Rev.*, 2009, **38**, 564-584):

$$c_n = K^{n-1}c_1^n$$

$$c = (c_1 + 2Kc_1^2 + 3K^2c_1^3 + \ldots + nK^{n-1}c_1^n)$$

$$c_1 = \frac{2Kc + 1 - \sqrt{4Kc+1}}{2K^2c}$$

$$\alpha_{agg} = Kc_1 = \frac{2Kc + 1 - \sqrt{4Kc+1}}{2Kc}$$

So the measured extinction coefficient (ε) at 325 nm as a function of concentration is fitted by the following equation defined by the isodesmic model:

$$\varepsilon = \varepsilon_{agg}\alpha_{agg} = \frac{\varepsilon_{agg}\,(2Kc + 1 - \sqrt{4Kc+1})}{2Kc}$$

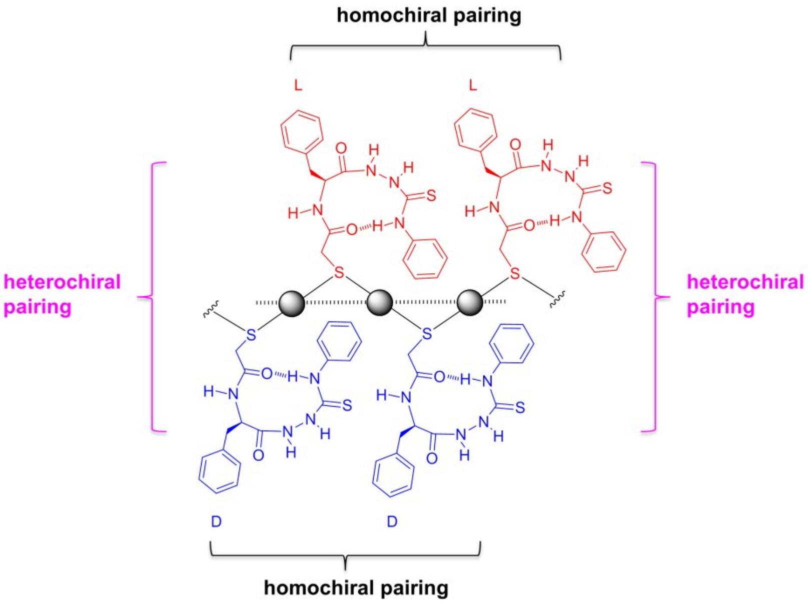


Fig. S17 Proposed structural model of the coordination polymers formed from racemic **TFTU** in the presence of Ag^+.

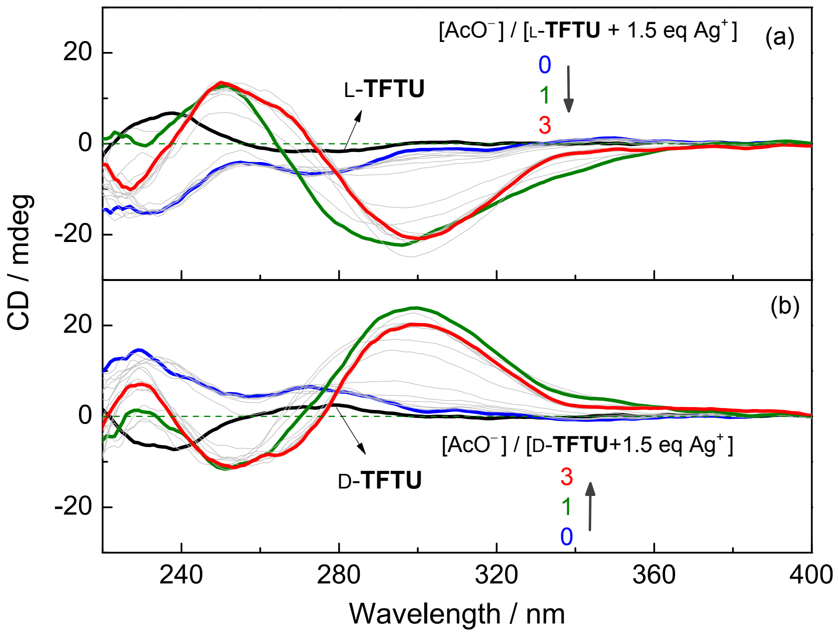


Fig. S18 CD spectra of **TFTU** with 1.5 equivalents of Ag^+ in the presence of AcO^- of increasing concentration from 0 to 3 equivalents. [L-**TFTU**] = [D-**TFTU**] = 100 μM, [$AgNO_3$] = 150 μM, [AcO^-] = 0 - 300 μM. AcO^- exists as the $(n\text{-Bu})_4N^+$ salt.

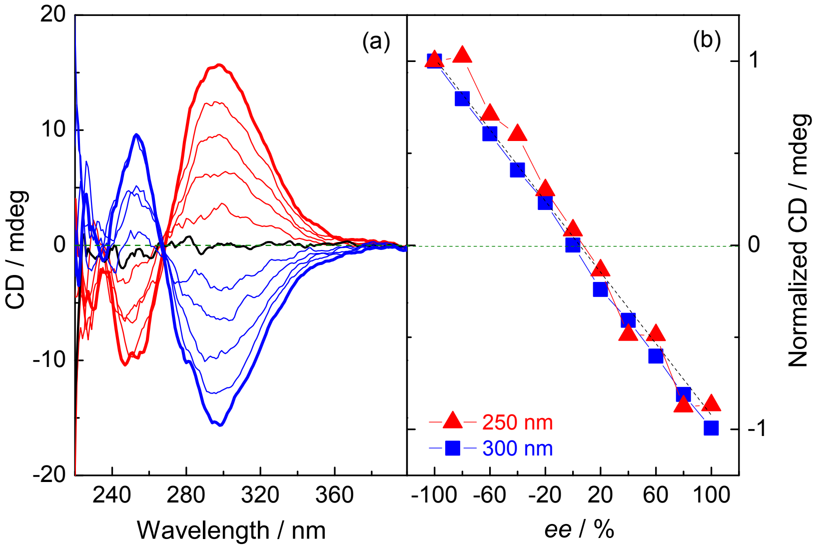


Fig. S19 (a) CD spectra of Ag^+-**TFTU** prepared from pure enantiomers in CH_3CN with varying *ee* in the presence of 1.5 equivalent AcO^- and (b) CD signals as a function of *ee* at 250 nm and 300 nm. [**TFTU**] = 100 μM. [$AgNO_3$] = [AcO^-] = 150 μM. AcO^- exists as the $(n\text{-Bu})_4N^+$ salt.

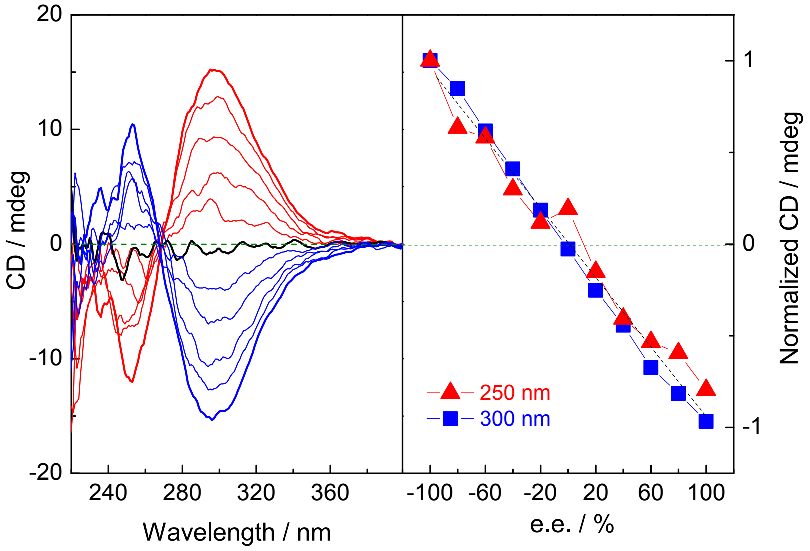


Fig. S20 (a) CD spectra of Ag$^+$-**TFTU** prepared from pure enantiomers in the presence of 1.5 equivalent AcO$^-$ after 1 hour in CH_3CN with varying *ee* and (b) CD signals as a function of *ee* at 250 nm and 300 nm. [**TFTU**] = 100 μM. [$AgNO_3$] = [AcO$^-$] = 150 μM. AcO$^-$ exists as the (*n*-Bu)$_4$N$^+$ salt.

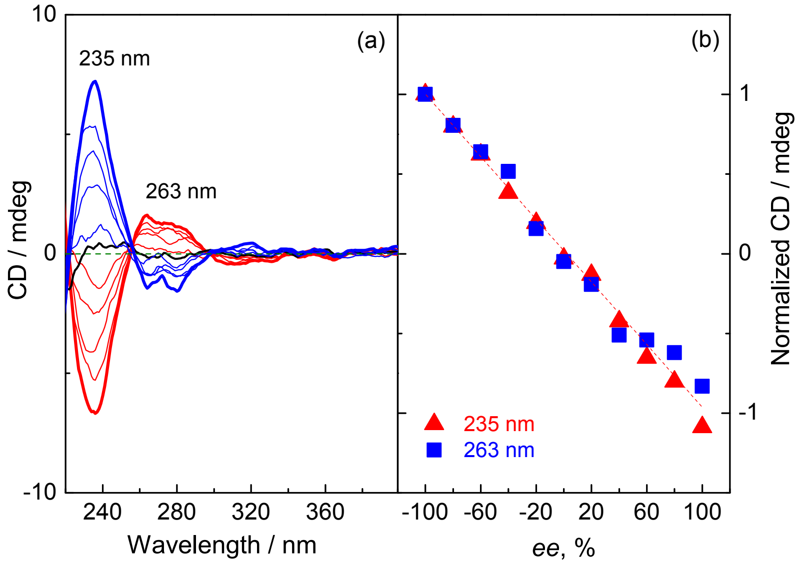


Fig. S21 (a) CD spectra in CH_3CN of **TFTU** of varying *ee* and (b) CD signals at 235 nm and 263 nm as a function of *ee*. [**TFTU**] = 100 μM.

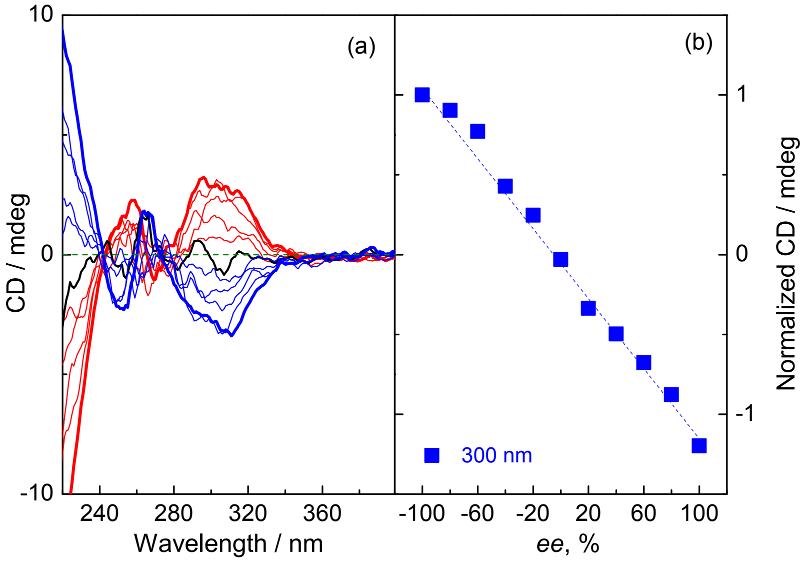


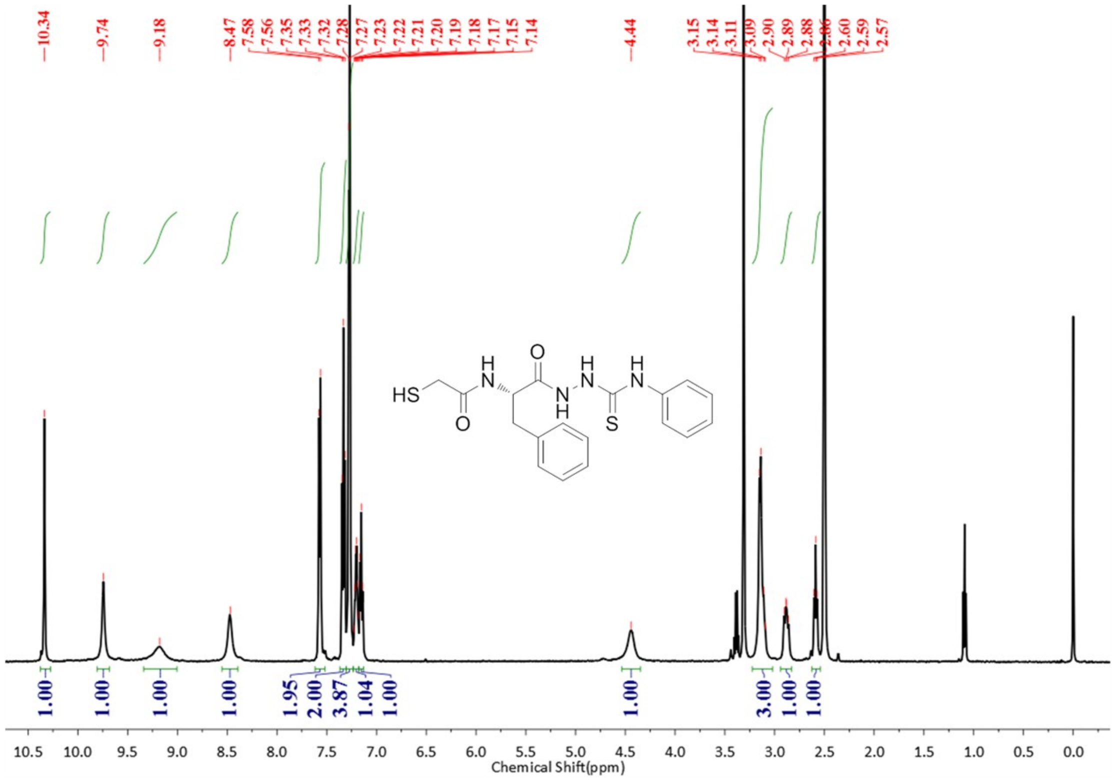
Fig. S22 (a) CD spectra in CH_3CN of **TFTU** of varying *ee* in the presence of 1.5 equivalents of AcO^- and (b) CD signals at 300 nm as a function of *ee*. [**TFTU**] = 100 μM. [AcO^-] = 150 μM. AcO^- exists as the $(n\text{-Bu})_4N^+$ salt.

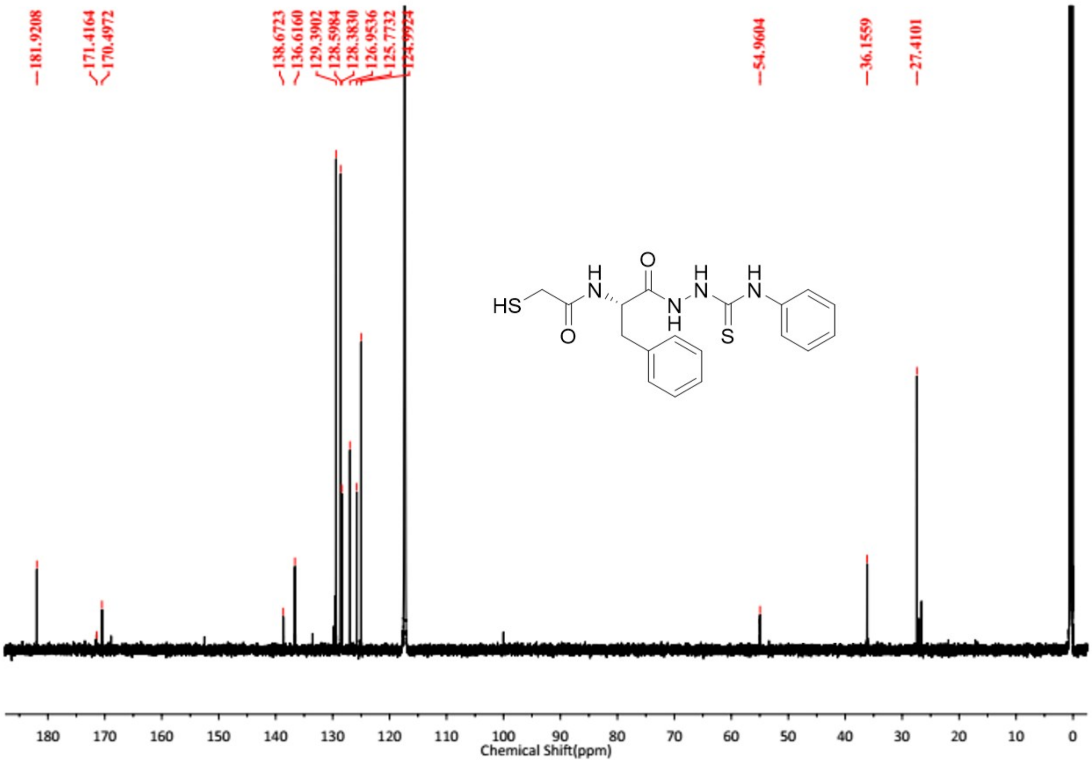
Table S1 Diffusion coefficients (D) and polymerization degrees (n) of **TFTU** and its complexes

Compound	**M_w**	**D (m^2/s)**	n
TFTU	388.50	$2.160*10^{-9}$	/
TFTU+1.0 eq. Ag^+	5455.65	$8.953*10^{-10}$	11.01
TFTU+1.0 eq. Ag^++1.0 eq. AcO^-	6949.76	$8.259*10^{-10}$	12.54

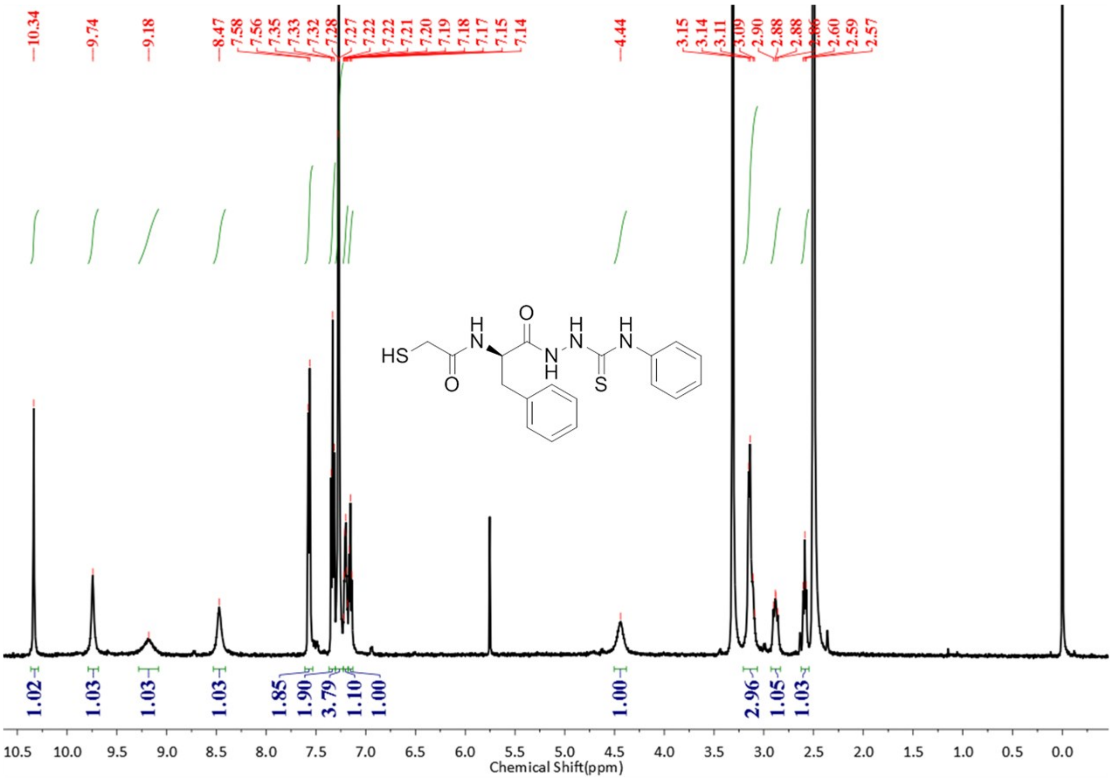
3. ^{1}H NMR and ^{13}C NMR spectra

L-TFTU





D-TFTU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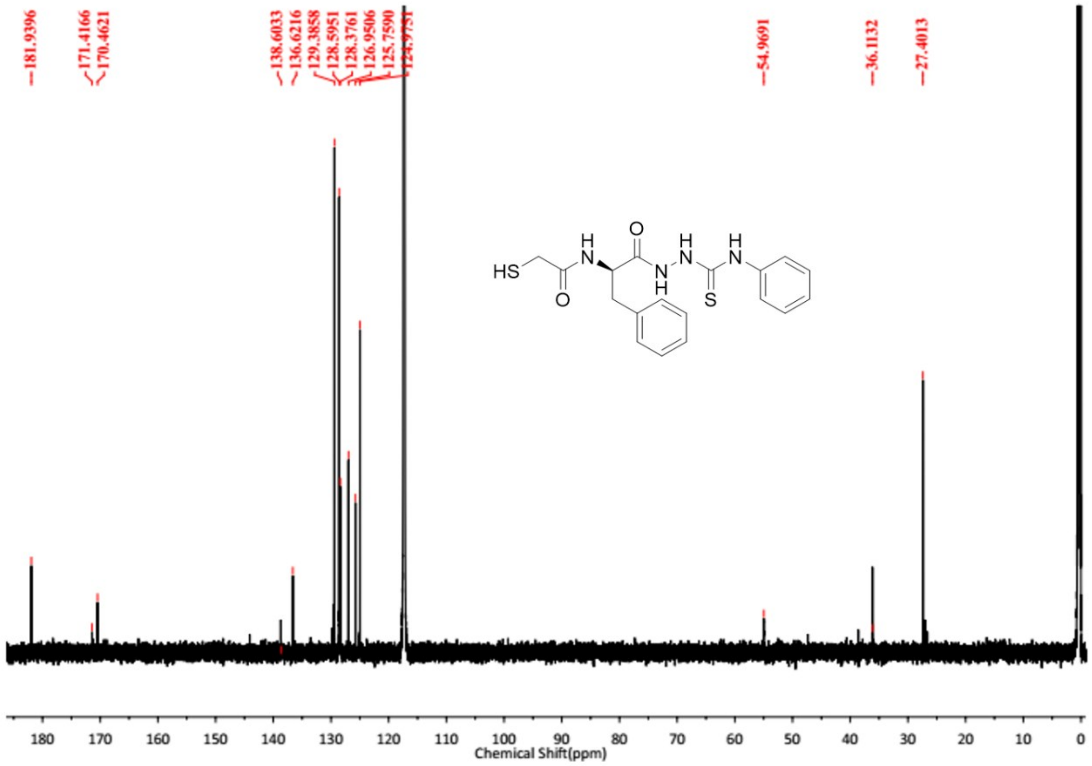
9.74
9.18
8.47
7.58
7.56
7.35
7.33
7.32
7.28
7.27
7.22
7.22
7.21
7.20
7.19
7.18
7.17
7.15
7.14
4.44
3.15
3.14
3.11
3.09
2.90
2.88
2.88
2.86
2.60
2.59
2.57
HS
N
H
O
O
N
H
N
H
S
N
H
1.02
1.03
1.03
1.03
1.85
1.90
3.79
1.10
1.00
1.00
2.96
1.05
1.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift(ppm)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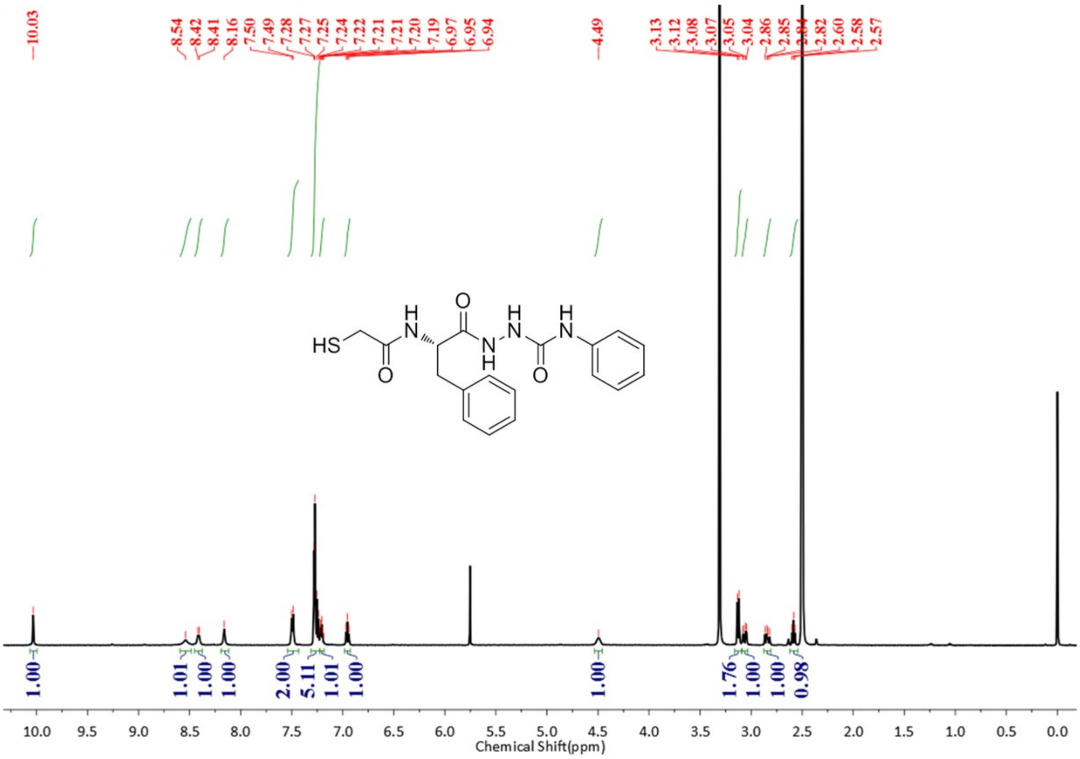
171.4166
170.4621
138.6033
136.6216
129.3858
128.5951
128.3761
126.9506
125.7590
124.9751
54.9691
36.1132
27.4013
HS
N
H
O
O
N
H
N
H
S
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift(ppm)

L-**TFU**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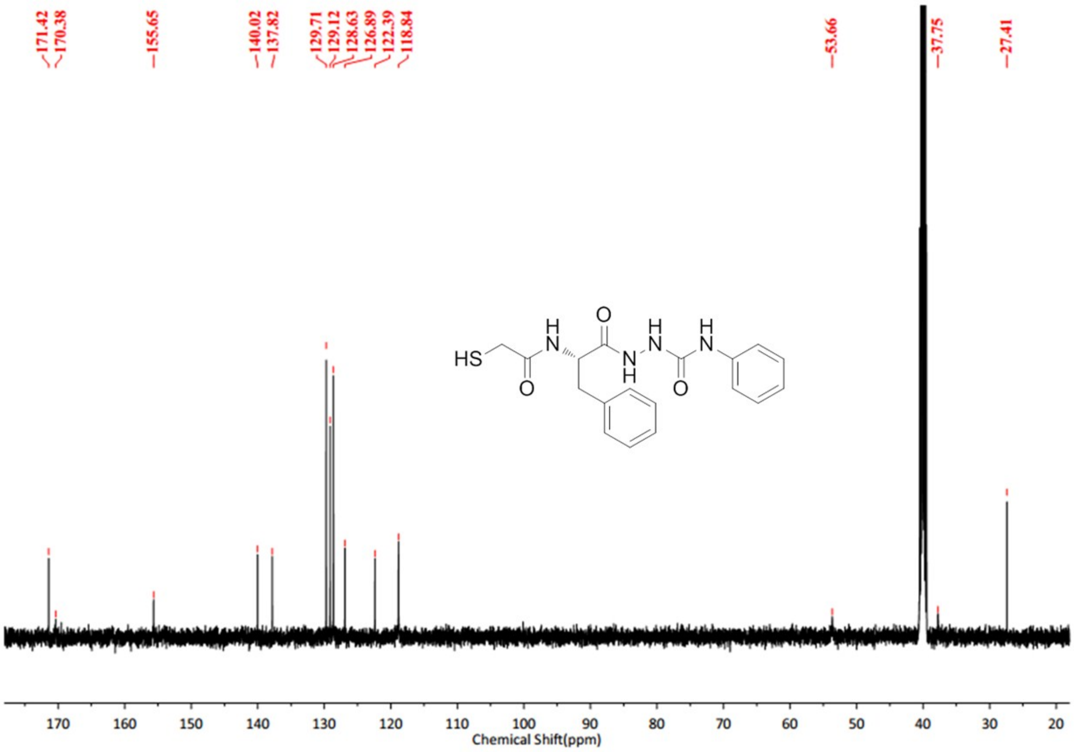
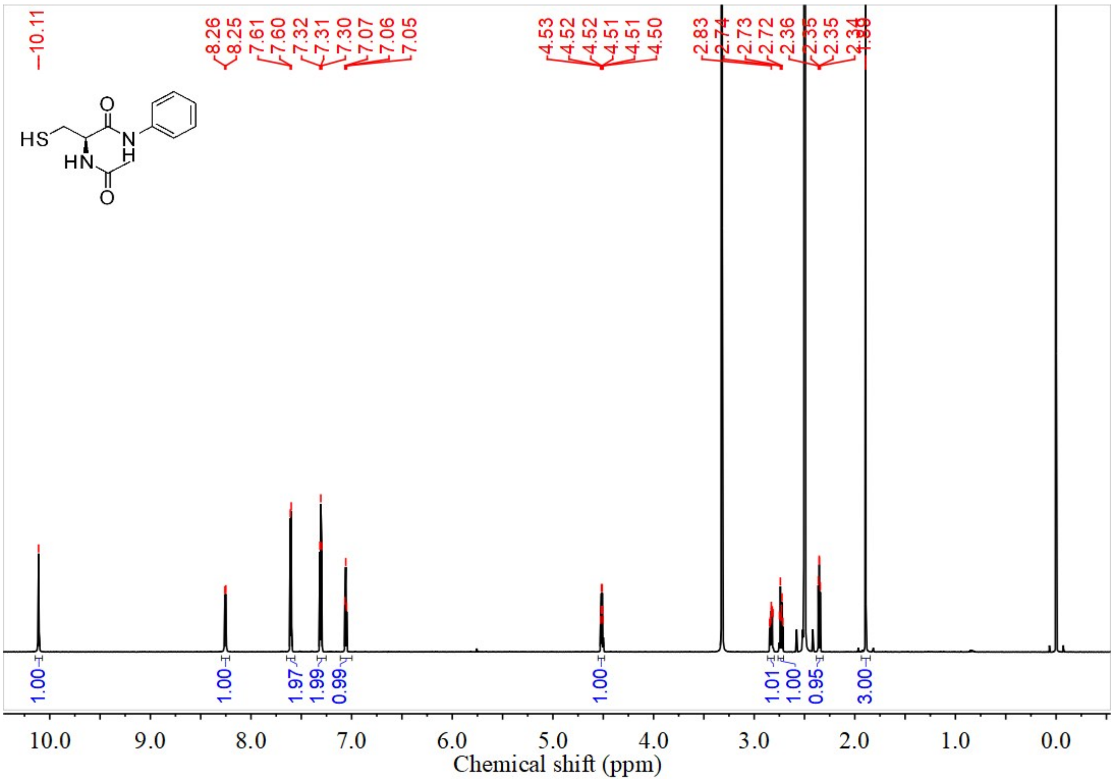
8.54
8.42
8.41
8.16
7.50
7.49
7.28
7.27
7.25
7.24
7.22
7.21
7.21
7.20
7.19
6.97
6.95
6.94
4.49
3.13
3.12
3.08
3.07
3.05
3.04
2.86
2.85
2.84
2.82
2.60
2.58
2.57
HS
H
N
O
H
N
N
H
O
H
N
O
1.00
1.01
1.00
1.00
2.00
5.11
1.01
1.00
1.00
1.76
1.00
1.00
0.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift(ppm)


171.42
170.38
155.65
140.02
137.82
129.71
129.12
128.63
126.89
122.39
118.84
53.66
37.75
27.41
HS
H
N
O
H
N
N
H
O
H
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
Chemical Shift(ppm)

L-NACA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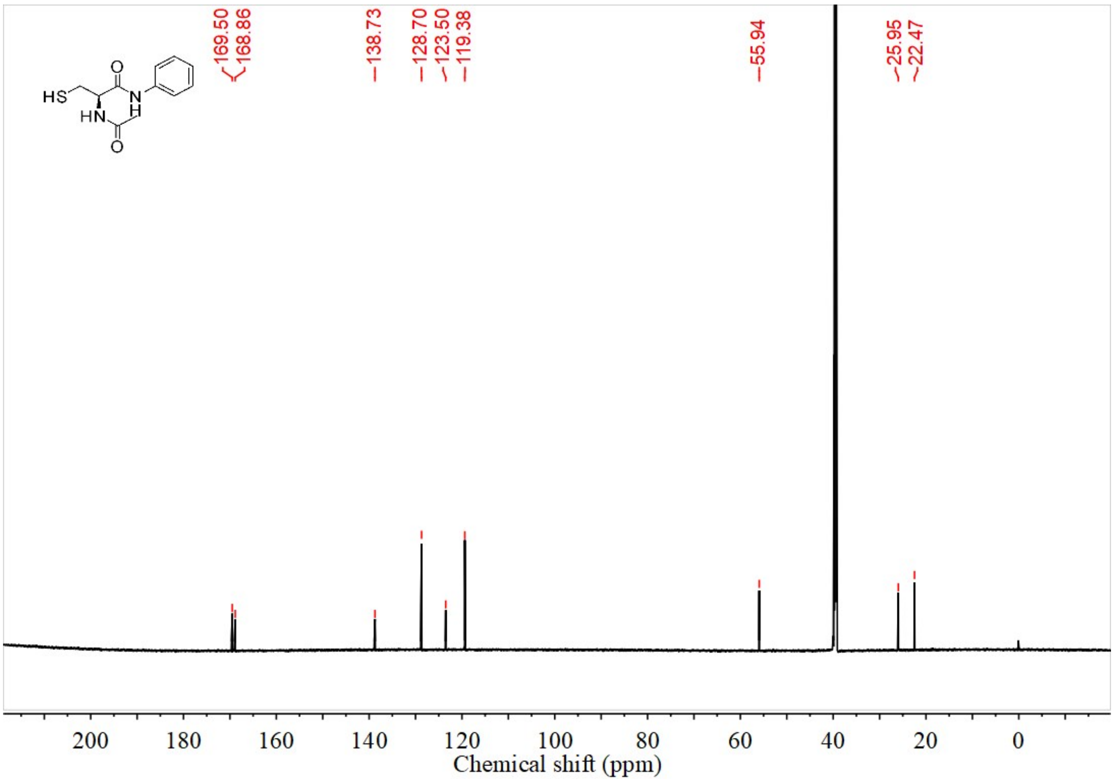
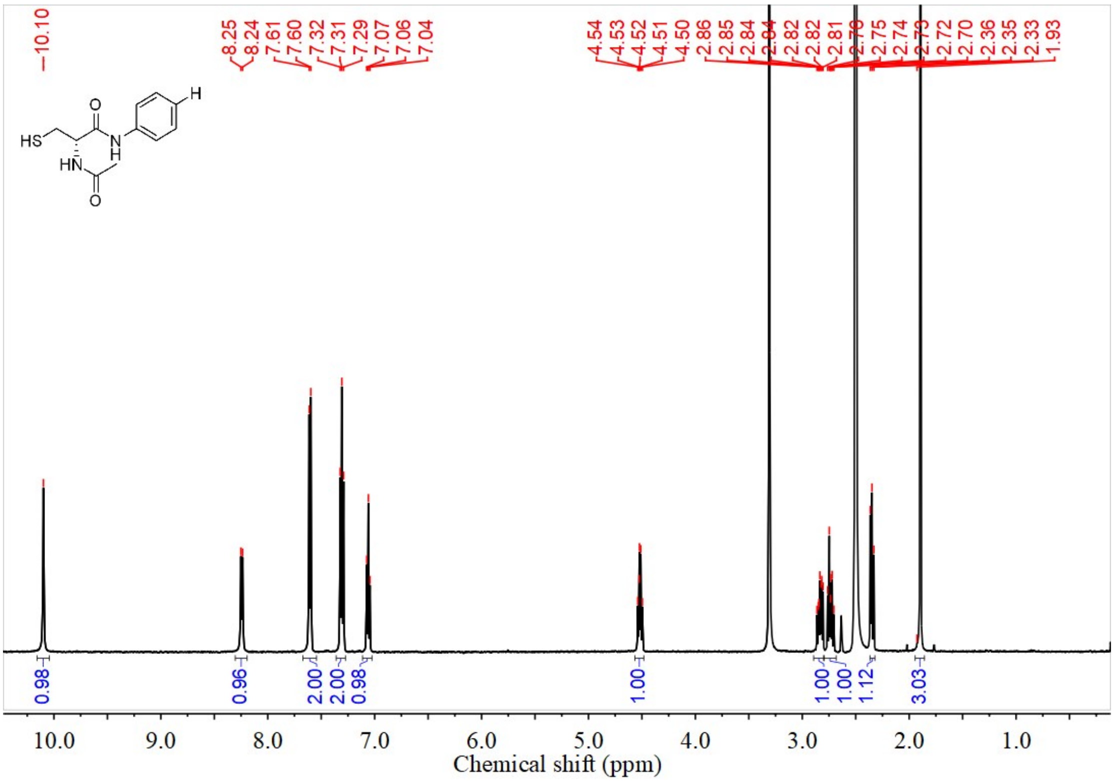
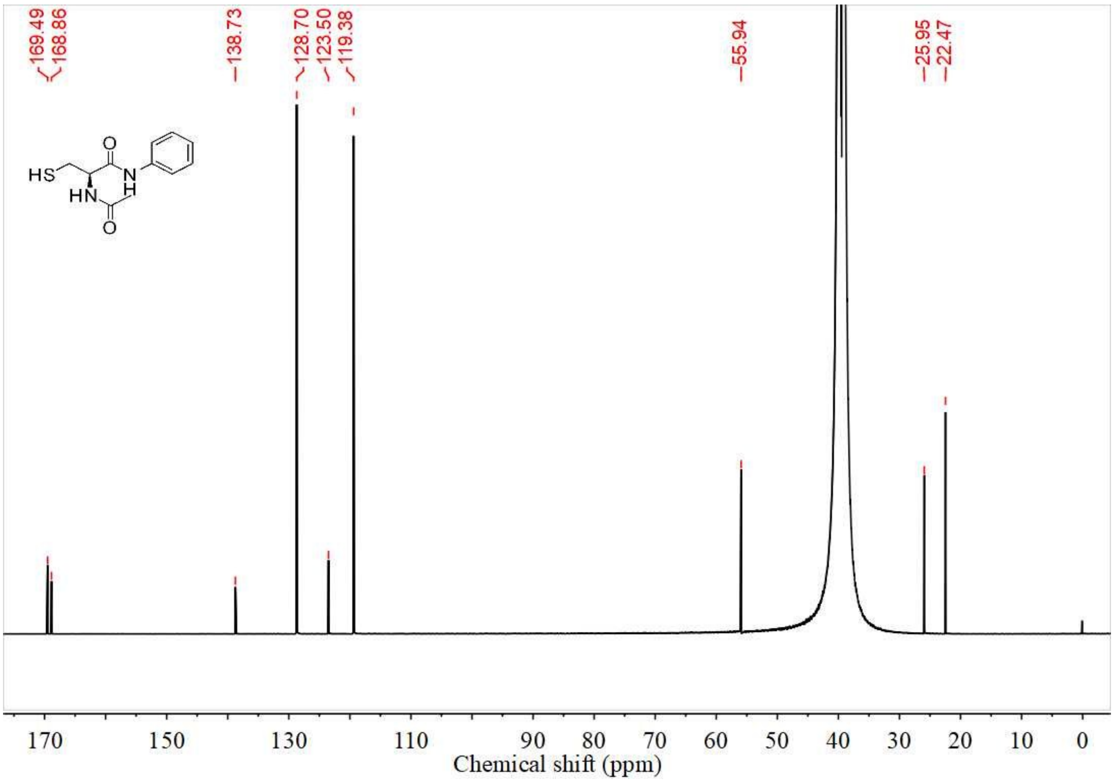
8.26
8.25
7.61
7.60
7.32
7.31
7.30
7.07
7.06
7.05
4.53
4.52
4.52
4.51
4.51
4.50
2.83
2.74
2.73
2.72
2.36
2.35
2.35
2.34
HS
O
N
H
HN
O
1.00
1.00
1.97
1.99
0.99
1.00
1.01
1.00
0.95
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)


169.50
168.86
138.73
128.70
123.50
119.38
55.94
25.95
22.47
HS
O
N
H
HN
O
200
180
160
140
120
100
80
60
40
20
0
Chemical shift (ppm)

D-**NACA**


10.10
8.25
8.24
7.61
7.60
7.32
7.31
7.29
7.07
7.06
7.04
4.54
4.53
4.52
4.51
4.50
2.86
2.85
2.84
2.82
2.82
2.81
2.75
2.74
2.72
2.70
2.36
2.35
2.33
1.93
HS
O
N
H
H
HN
O
0.98
0.96
2.00
2.00
0.98
1.00
1.00
1.00
1.12
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical shift (ppm)


169.49
168.86
138.73
128.70
123.50
119.38
55.94
25.95
22.47
HS
O
N
H
HN
O
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)