Electronic Supplementary Information

Encapsulated oligothiophenes having electron-affinity characteristics

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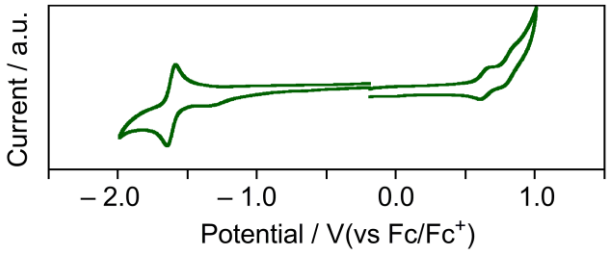


Fig. S1 CV of **h(TC$_m$T)$_2$h** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ as a supporting electrolyte.

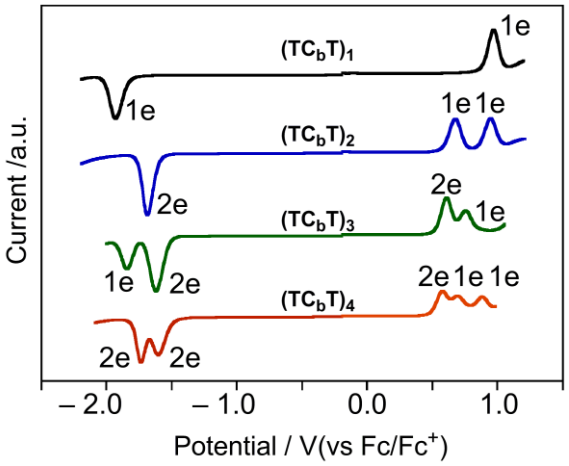


Fig. S2 DPVs of oligothiophenes in CH_2Cl_2 containing 0.1 M $TBAPF_6$ as a supporting electrolyte.

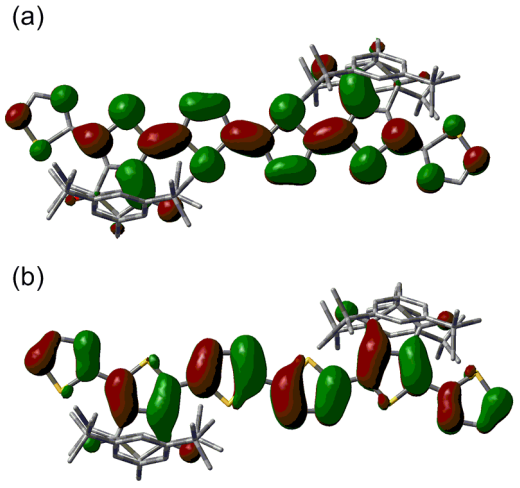


Fig. S3 Calculated frontier orbitals of LUMO (a) and HOMO (b) for **(TC$_b$T)$_2$**.

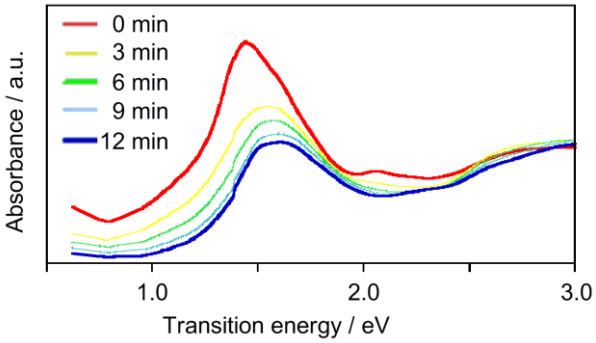


Fig. S4 UV-vis-NIR spectra of the dianionic species of $\mathbf{(TC_bT)_2}$. These measurements were performed by treatment of $\mathbf{(TC_bT)_2}$ with K/graphite in THF at room temperature under inert conditions. According to time-dependent DFT calculations of dianionic species at the long-range corrected (LC)-BLYP/6-31+G(d,p) level, the observed band at 1.44 eV can be mainly ascribed to the HOMO–LUMO transition.

The calculated excited state of dianionic species of $\mathbf{(TC_bT)_2}$ at LC-BLYP/6-31+G(d, p) level.

Excited State 1: 1.49 eV (831 nm): oscillator strength *(f)* =1.76

HOMO–1 – LUMO+1	0.18875
HOMO – LUMO	0.63891

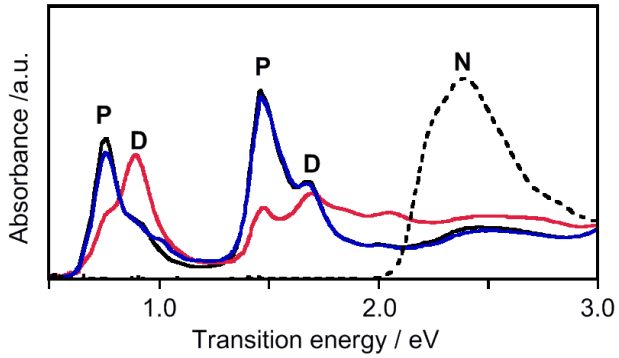


Fig. S5 UV-vis-NIR spectra of $\mathbf{h(TC_mT)_2h}$ (dashed line) and $\mathbf{h(TC_mT)_2h^{\bullet+}}$ (black line : r.t. red line : 233K. blue line : after warming to r.t.). N, P, and D denote neutral, polaronic, and π-dimeric bands, respectively.

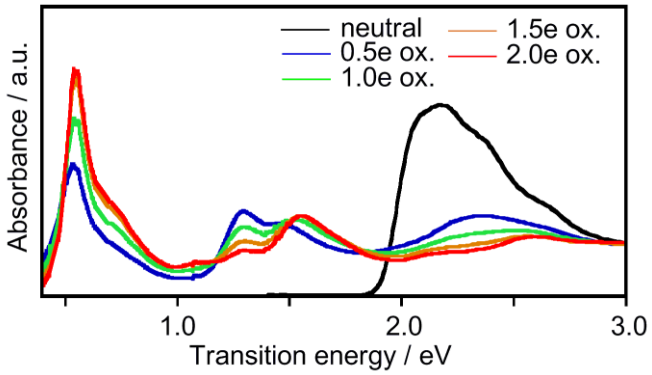


Fig. S6 UV-vis-NIR spectra of **$(TC_bT)_4$** with successive oxidation in CH_2Cl_2.

General Information. Column chromatography was performed on silica gel, KANTO Chemical silica gel 60N (40–50 μm). Thin-layer chromatography (TLC) plates were visualized with UV light. Preparative gel-permeation chromatography (GPC) was performed on Japan Analytical Industry LC-918 equipped with JAI-GEL 1H/2H or 2.5H/3H columns. Analytical GPC was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a shodex K-803L. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 or ECA-600 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), and integration. Mass spectra were obtained on a Shimadzu GCMS-QP-5050 or a Shimadzu AXIMA-TOF. UV-vis-NIR spectra were recorded on a Shimadzu UV-3100PC spectrophotometer equipped with nonfocused optics in an environmental chamber Oxford Optistat-DN cryostat. All spectra were obtained in spectrograde solvents. Cyclic voltammetry was carried out on a BAS CV-620C voltammetric analyzer. High resolution mass spectrum (HRMS) was obtained on Brucker ultraflex III. Elemental analyses were performed on Perkin Elmer LS-50B by the Elemental Analysis Section of CAC, ISIR, Osaka University.

Materials. All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. 1,3-dibromo-4*H*-cyclopenta[*c*]thiophene-4,6(5*H*)-dione (**1**)[1], 3,5-di-*t*-butylbenzylbromide[2], and 2-hexyl-5-tributylstannylthiophene[3] were prepared by reported procedures, and ^{1}H NMR data of these compound were in agreement with those previously reported.

Experimental Procedure

Synthesis of ***2***: **1** (1.55 g, 5.00 mmol) and 3,5-di-*t*-butylbenzylbromide (8.50 g, 30.0 mmol) were placed in a test tube with screw cap and dissolved in acetonitrile (25 mL). 50 wt% KF on celite (3.47 g, 29.9 mmol) was added, and the resulting mixture was stirred at 70 ºC for 12 h. After being cooled to room temperature, the mixture was filtered over celite. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/$CHCl_3$ = 3/1) to give **2** (2.38 g, 67%).

Colorless solid; TLC: R_f = 0.16 (hexane/$CHCl_3$ = 3/1); Mp: 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (s, 18H), 3.25 (s, 4H), 6.82 (d, *J* = 2.0 Hz, 4H), 7.06 (t, *J* = 2.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.3, 34.6, 42.7, 72.2, 110.6, 120.3, 124.2, 134.2 145.3, 150.6, 194.4; MS (DI): *m/z* = 714 (M^+); Anal. Calcd for $C_{37}H_{46}Br_2O_2S$: C, 62.19; H, 6.49. Found: C, 62.06; H, 6.52.

Synthesis of ***(TC$_b$T)$_1$***: **2** (970 mg, 1.36 mmol), 2-tributylstannylthiophene (1.52 g, 4.07 mmol), and $Pd(PPh_3)_4$ (155 mg, 0.135 mol) were placed in a test tube with screw cap and dissolved in toluene (15 mL). The reaction mixture was stirred at 120 ºC for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina (hexane/$CHCl_3$ = 3/1) to give **(TC$_b$T)$_1$** (910 mg, 93%).

Yellow solid; TLC: R_f = 0.42 (hexane/$CHCl_3$ = 3/1); Mp: 233-235 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (s, 18H), 3.29 (s, 4H), 6.85 (d, *J* = 2.0 Hz, 4H), 6.99 (t, *J* = 2.0 Hz, 2H), 7.05 (dd, *J* = 4.8, 3.6 Hz, 2H), 7.35 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.95 (dd, *J* = 3.6, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.1, 34.5, 43.0, 72.2, 120.2, 124.2, 128.1, 128.4, 129.5, 133.0, 134.7, 135.1, 140.6, 150.3, 195.8; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 719.7 (M^+, Calcd 720.3); Anal. Calcd for $C_{45}H_{52}O_2S_3$: C, 74.95; H, 7.27. Found: C, 74.97; H, 7.28.

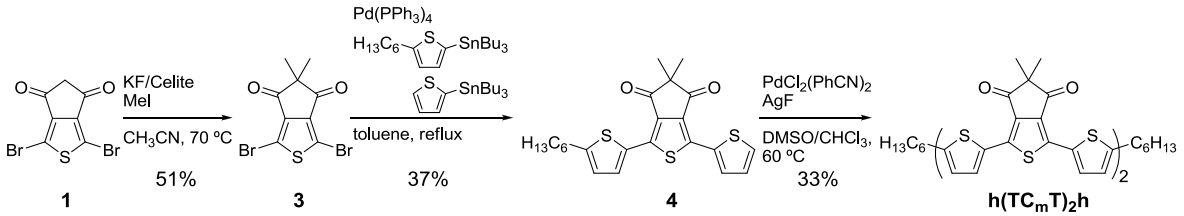
Synthesis of ***(TC$_b$T)$_n$***: **(TC$_b$T)$_1$** (360 mg, 0.499 mmol), $PdCl_2(PhCN)_2$ (19 mg, 50 μmol), and AgF (254 mg, 2.00 mmol) were placed in a test tube with screw cap and dissolved in DMSO (1.6 mL) and $CHCl_3$ (0.8 mL). After stirring for 12 h at 60 ºC, the reaction mixture was quenched by addition of NaCl aq.. The reaction mixture was filtered over celite, and the organic layer was separated. The organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was filtered over alumina with $CHCl_3$ as eluent, followed by purification with preparative GPC

(JAIGEL 2.5H/3H, $CHCl_3$) to give **$(TC_bT)_2$** (96 mg, 27%), **$(TC_bT)_3$** (82 mg, 23%), and **$(TC_bT)_4$** (32 mg, 9%).

$(TC_bT)_2$: Red solid; Mp: > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 72H), 3.31 (s, 8H), 6.87 (d, *J* = 2.0 Hz, 8H), 7.01 (t, *J* = 2.0 Hz, 4H), 7.08 (dd, *J* = 4.8, 3.6 Hz, 2H), 7.19 (d, *J* = 3.6 Hz, 2H), 7.38 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.89 (d, *J* = 3.6 Hz, 2H), 7.97 (dd, *J* = 3.6, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.1, 34.5, 43.0, 72.3, 120.2, 124.2, 125.3, 128.2, 128.6, 129.7, 130.5, 132.7, 132.9, 134.1, 134.6, 135.3, 139.1, 140.8, 141.0, 150.4, 195.7, 195.9; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 1438.1 (M^+, Calcd 1438.6); Anal. Calcd for $C_{90}H_{102}O_4S_6$: C, 75.06; H, 7.14. Found: C, 74.67; H, 7.17.

$(TC_bT)_3$: Dark purple solid; Mp: > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 72H), 1.10 (s, 36H), 3.32 (s, 8H), 3.33 (s, 4H), 6.88 (d, *J* = 2.0 Hz, 8H), 6.89 (d, *J* = 2.0 Hz, 4H), 7.02 (t, *J* = 2.0 Hz, 4H), 7.03 (t, *J* = 2.0 Hz, 2H), 7.08 (dd, *J* = 4.8, 3.6 Hz, 2H), 7.21 (d, *J* = 3.6 Hz, 4H), 7.38 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.90 (d, *J* = 3.6 Hz, 2H), 7.91 (d, *J* = 3.6 Hz, 2H), 7.98 (dd, *J* = 3.6, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.3, 31.3, 34.6, 34.6, 43.1, 72.4, 120.3, 120.4, 124.3, 125.5, 125.6, 128.4, 128.8, 129.8, 130.6, 130.8, 132.7, 132.9, 133.0, 134.1, 134.4, 134.7, 135.5, 139.1, 139.5, 140.9, 141.2, 141.2, 150.5, 150.5, 195.8, 195.9, 196.0; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 2156.6 (M^+, Calcd 2156.9); Anal. Calcd for $C_{135}H_{152}O_6S_9$: C, 75.09; H, 7.10. Found: C, 74.83; H, 7.16.

$(TC_bT)_4$: Dark violet solid; Mp: > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 72H), 1.10 (s, 72H), 3.31 (s, 8H), 3.33 (s, 8H), 6.87 (d, *J* = 1.6 Hz, 8H), 6.89 (d, *J* = 1.6 Hz, 8H), 7.01 (t, *J* = 1.6 Hz, 4H), 7.03 (t, *J* = 1.6 Hz, 4H), 7.07 (dd, *J* = 4.8, 3.6 Hz, 2H), 7.21 (m, 6H), 7.37 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.90 (m, 6H), 7.97 (dd, *J* = 3.6, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.2, 31.2, 34.5, 34.5, 43.0, 72.3, 120.2, 120.3, 124.2, 125.4, 125.5, 128.3, 128.7, 129.7, 130.5, 130.7, 132.6, 132.7, 132.8, 132.9, 134.0, 134.2, 134.3, 134.6, 135.4, 139.0, 139.3, 139.4, 140.8, 141.1, 141.2, 141.2, 150.4, 150.4, 195.7, 195.8, 195.8, 195.9; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 2874.6 (M^+, Calcd 2875.2); Exact mass Calcd for $C_{180}H_{202}O_8S_{12}$: 2875.205. Found: 2875.194.



Scheme S1. Synthesis of **h(TC$_m$T)$_2$h**.

*Synthesis of **3***: **1** (660 mg, 2.13 mmol) and iodomethane (1.81 g, 12.8 mmol) were placed in a test tube with screw cap and dissolved with acetonitrile (10 mL). 50 wt% KF on celite (1.49 g, 12.8 mmol) was added and the resulting mixture was stirred at 70 ºC for 12 h. After being cooled to room temperature, the mixture was filtered over celite. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/$CHCl_3$ = 2/1) to give **3** (370 mg, 51%).

Colorless solid; Mp: 202-204 °C; TLC: R_f = 0.40 (hexane/$CHCl_3$ = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.9, 59.5, 113.4, 143.1, 194.6; MS (DI): *m/z* = 338 (M^+); Anal. Calcd for $C_9H_6Br_2O_2S$: C, 31.98; H, 1.79. Found: C, 31.98; H, 2.02.

*Synthesis of **4***: **3** (200 mg, 0.575 mmol), 2-tributylstannylthiophene (257 mg, 0.690 mmol), 2-hexyl-5-tributylstannyl thiophene (316 mg, 0.690 mmol), and $Pd(PPh_3)_4$ (67 mg, 58 μmol) were placed in a test tube with screw cap and dissolved in toluene (6 mL). The resulting mixture was stirred at 120 ºC for 12 h. After removal of the solvent under reduced pressure, the residue was filtered over alumina with $CHCl_3$ as eluent, followed by purification with preparative GPC (JAIGEL 1H/2H, $CHCl_3$) to give **4** (91 mg, 37 %).

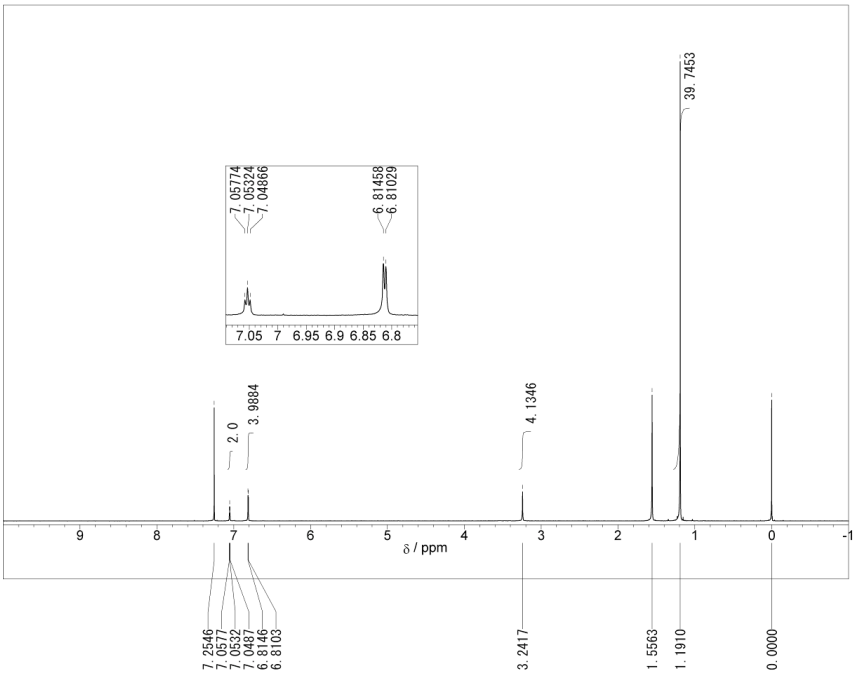
Yellow solid; Mp: 99-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.28-1.44(m, 6H), 1.36(s, 6H), 1.72 (m, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 3.6 Hz, 1H), 7.13 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.43 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.93 (d, *J* = 3.6 Hz, 1H), 8.07 (dd, *J* = 3.6, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.1, 21.3, 22.6, 28.8, 30.3, 31.5, 31.5, 59.6, 125.8, 128.4, 128.6, 129.7, 130.2, 130.5, 133.1, 136.4, 137.2, 138.0, 138.1, 150.9, 196.5, 196.7; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 427.4 (M^+, Calcd 428.1); Anal. Calcd for $C_{23}H_{24}O_2S_3$: C, 64.45; H, 5.64. Found: C, 64.17; H, 5.58.

Synthesis of ***h(TC$_m$T)$_2$h***: **4** (91 mg, 0.21 mmol), AgF (107 mg, 0.85 mmol), and $PdCl_2(PhCN)_2$ (8.1 mg, 21 μmol) were placed in a test tube with screw cap and dissolved in DMSO (1.0 mL) and $CHCl_3$ (0.5 mL). After stirring for 12 h at 60 ºC, the reaction mixture was quenched by addition of NaCl aq.. The reaction mixture was filtered over celite, and the organic layer was separated. The organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was filtered over alumina with $CHCl_3$ as eluent, followed by purification with preparative GPC (JAIGEL 1H/2H, $CHCl_3$) to give **h(TC$_m$T)$_2$h** (30 mg, 33%).

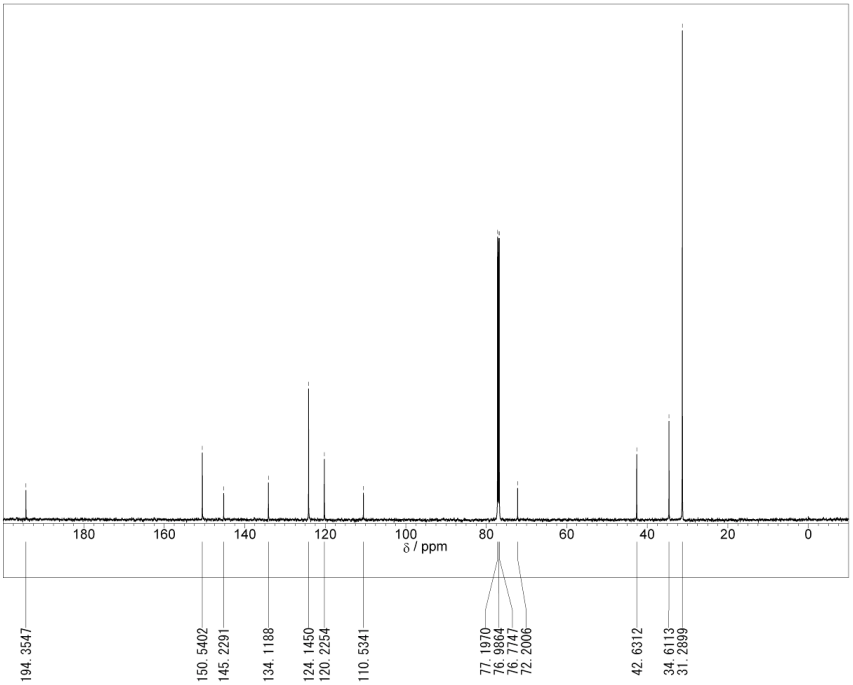
Dark violet solid; Mp: 287-289 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.2 Hz, 6H), 1.28-1.46 (m, 12H), 1.37 (s, 12H), 1.73 (m, 4H), 2.85 (t, *J* = 7.6 Hz, 4H), 6.81 (d, *J* = 3.6 Hz, 2H), 7.26 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.94 (d, *J* = 3.6 Hz, 2H), 7.99 (d, *J* = 3.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ = 1/2): δ 14.4, 21.4, 23.0, 29.2, 30.7, 31.8, 31.9, 59.6, 125.9, 126.2, 130.7, 131.0, 133.2, 135.5, 137.6, 138.4, 138.6, 139.5, 151.2, 196.1, 196.5; MS (MALDI-TOF,1,8,9-trihydroxyanthracene matrix) *m/z* 853.4 (M^+, Calcd 854.2); Exact mass Calcd for $C_{46}H_{46}O_4S_6$: 854.1707, Found: 854.1720.

NMR Spectra

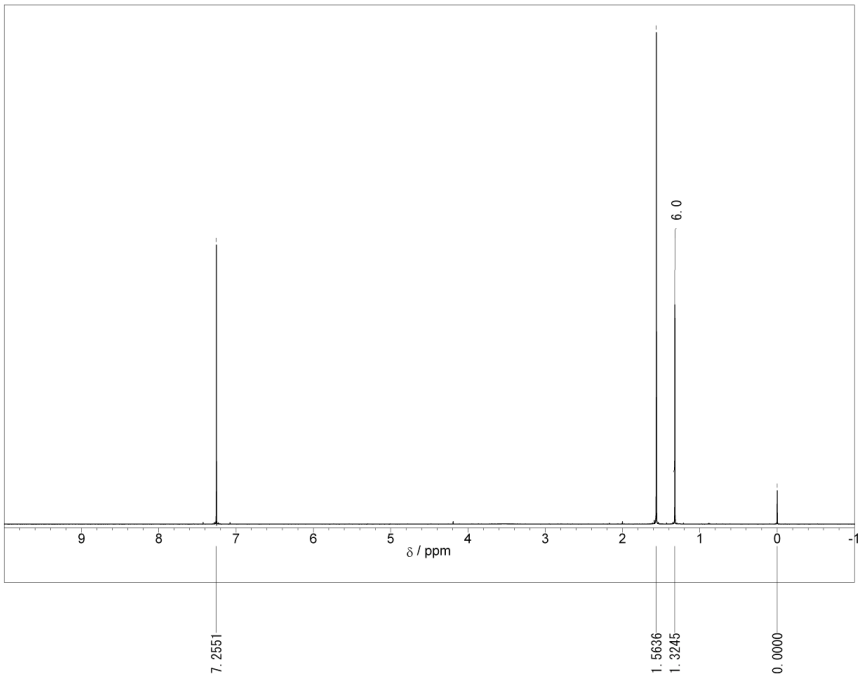
^{1}H NMR spectrum of **2**



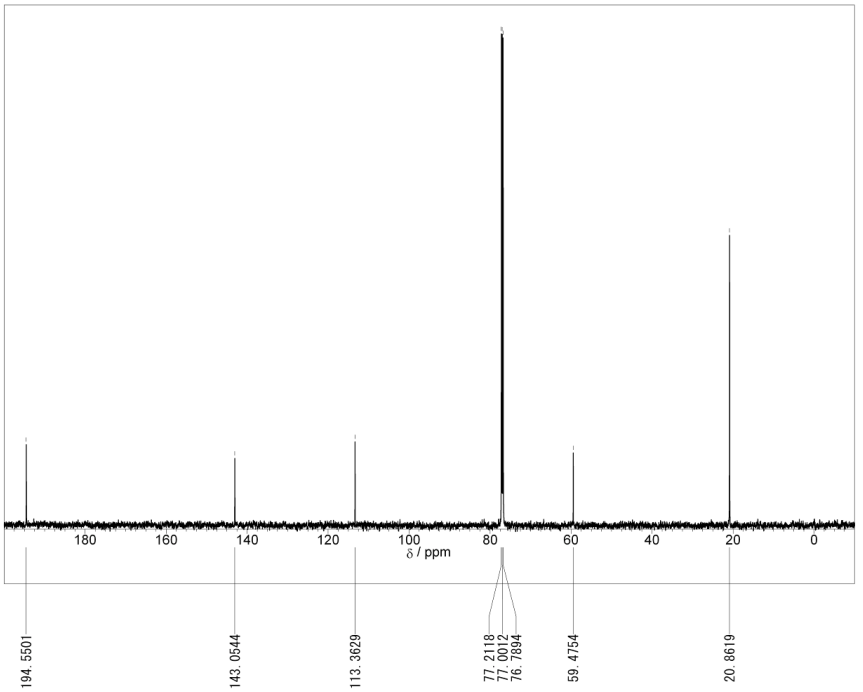
^{13}C NMR spectrum of **2**



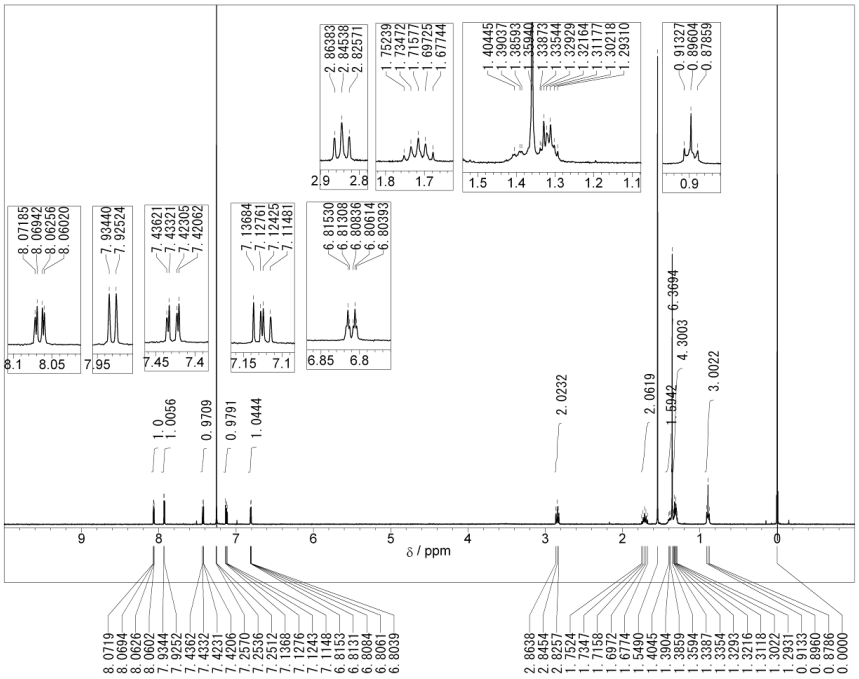
^{1}H NMR spectrum of **3**



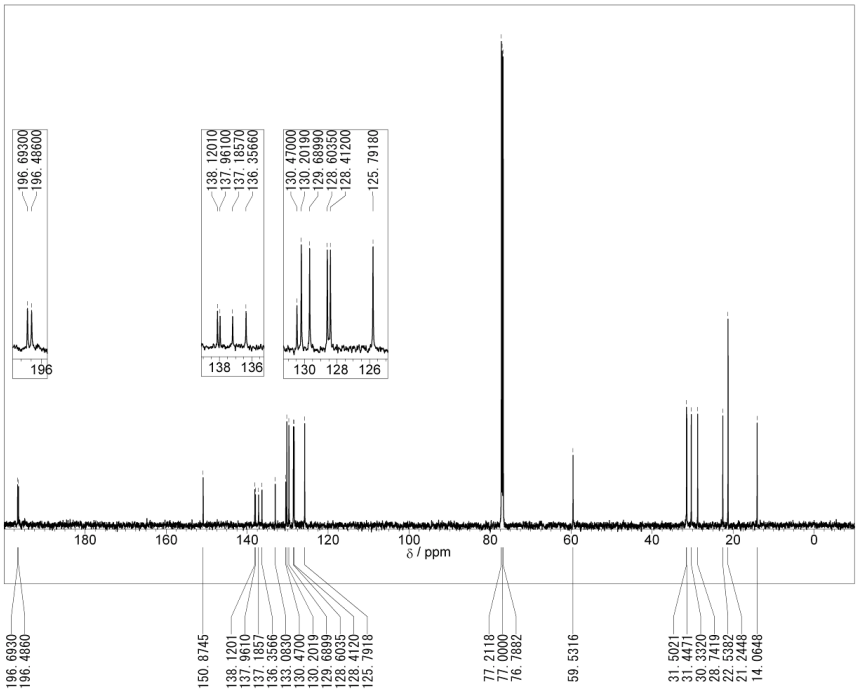
^{13}C NMR spectrum of **3**



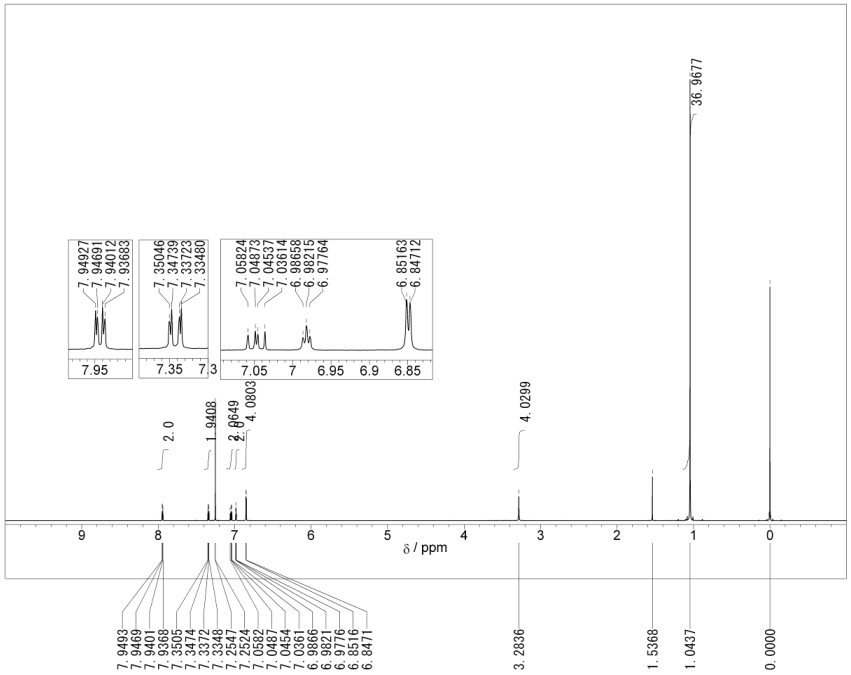
^{1}H NMR spectrum of **4**



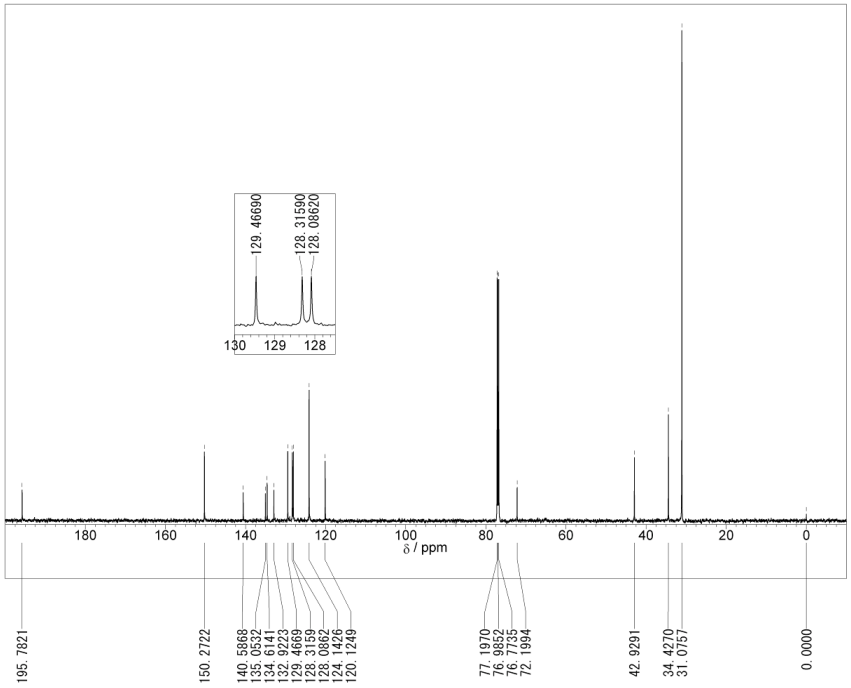
^{13}C NMR spectrum of **4**



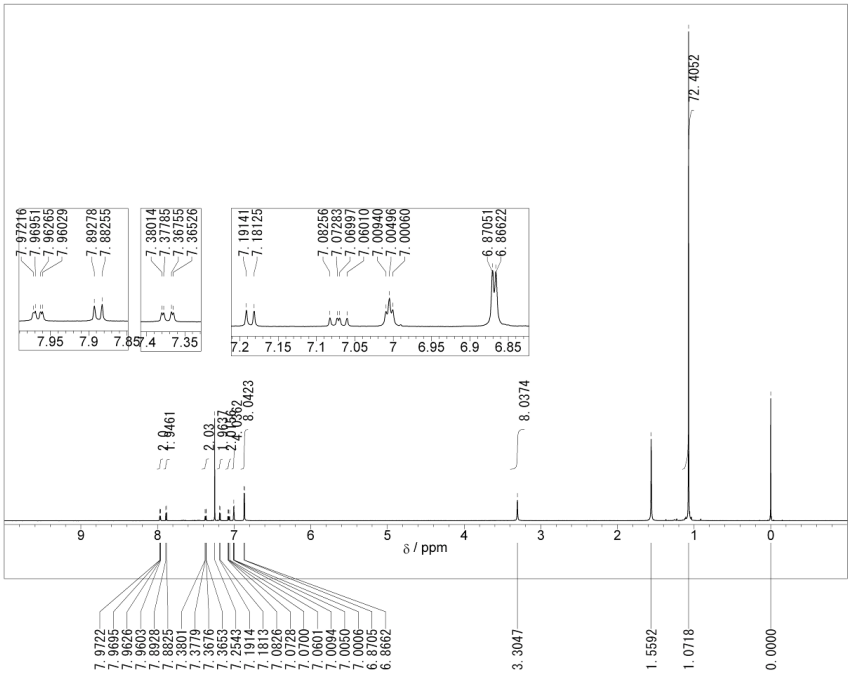
^{1}H NMR spectrum of **$(TC_bT)_1$**



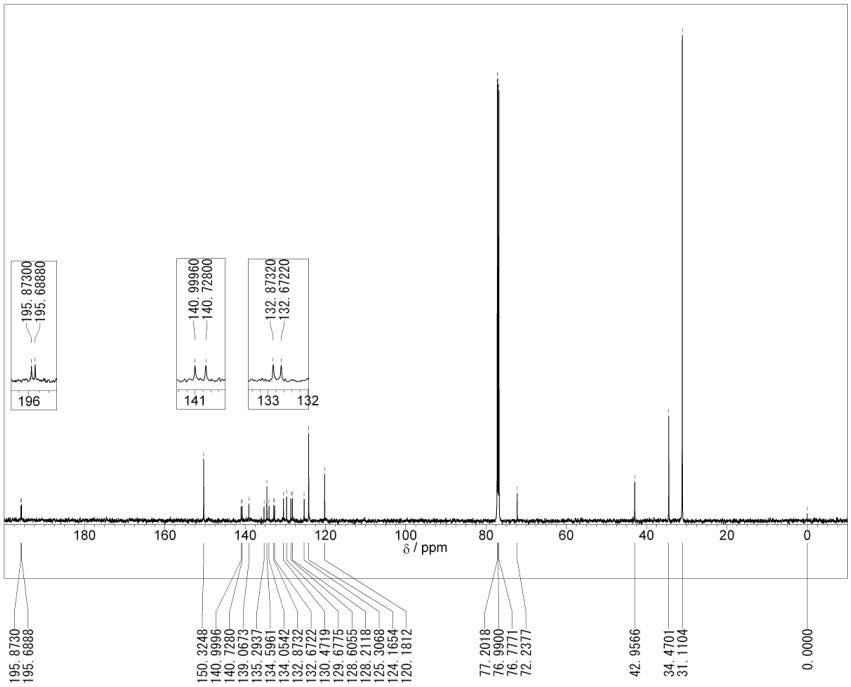
^{13}C NMR spectrum of **$(TC_bT)_1$**



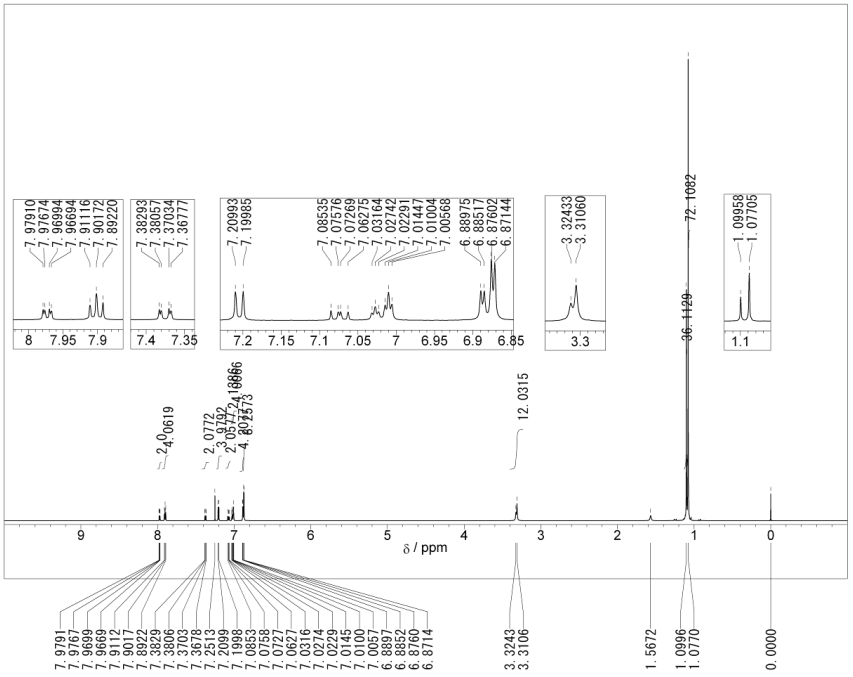
^{1}H NMR spectrum of **$(TC_bT)_2$**



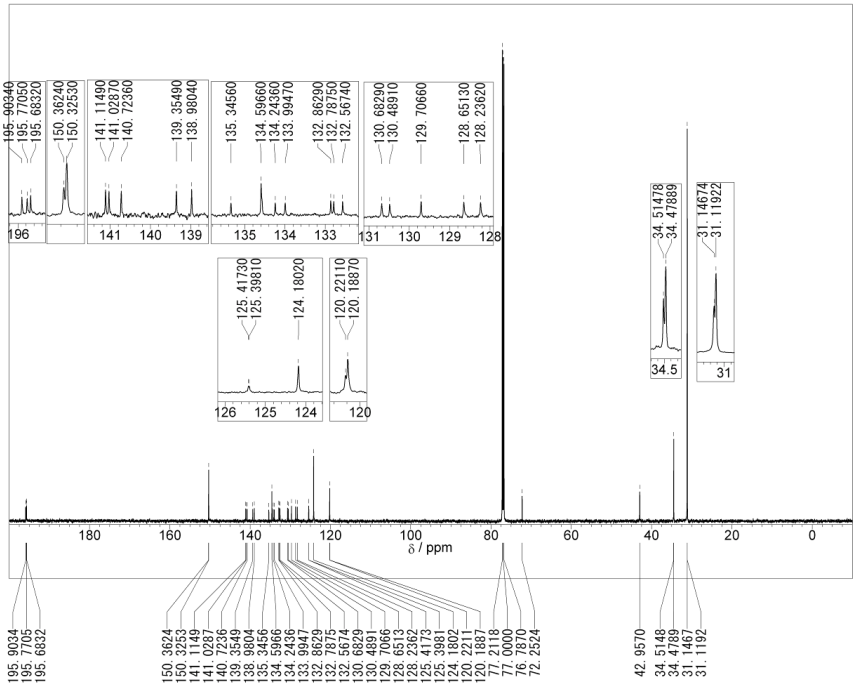
^{13}C NMR spectrum of **$(TC_bT)_2$**



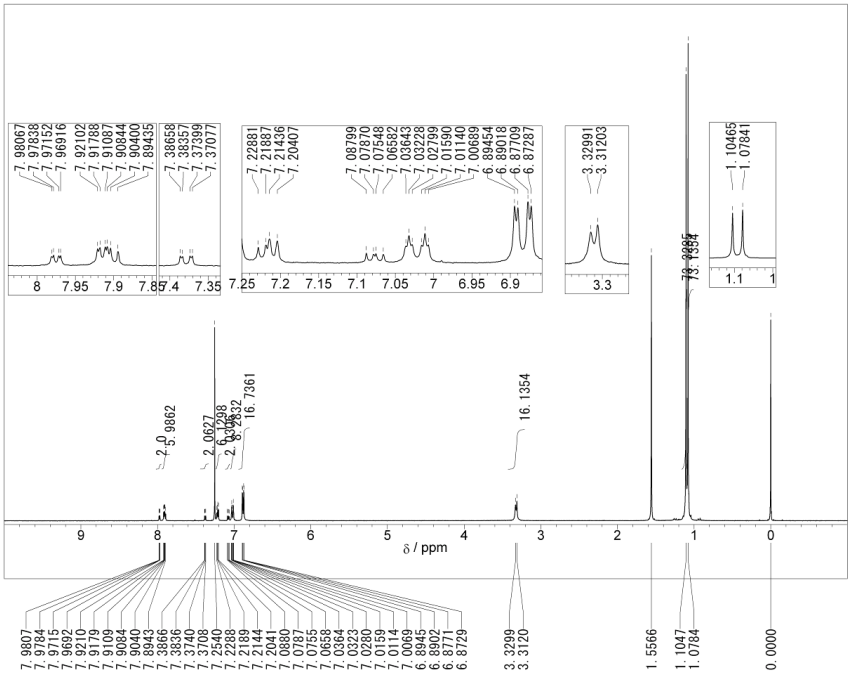
^{1}H NMR spectrum of **$(TC_bT)_3$**



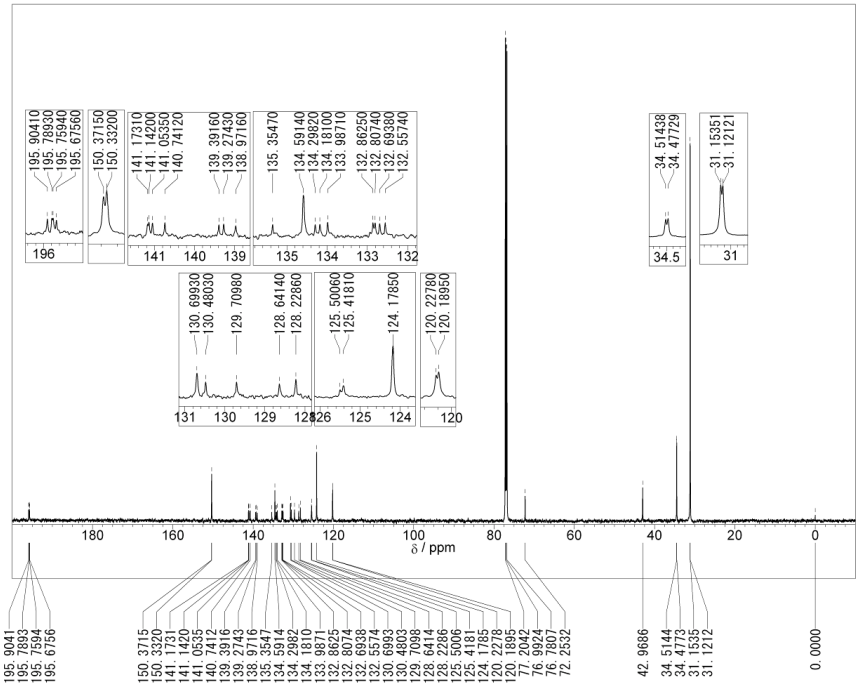
^{13}C NMR spectrum of **$(TC_bT)_3$**



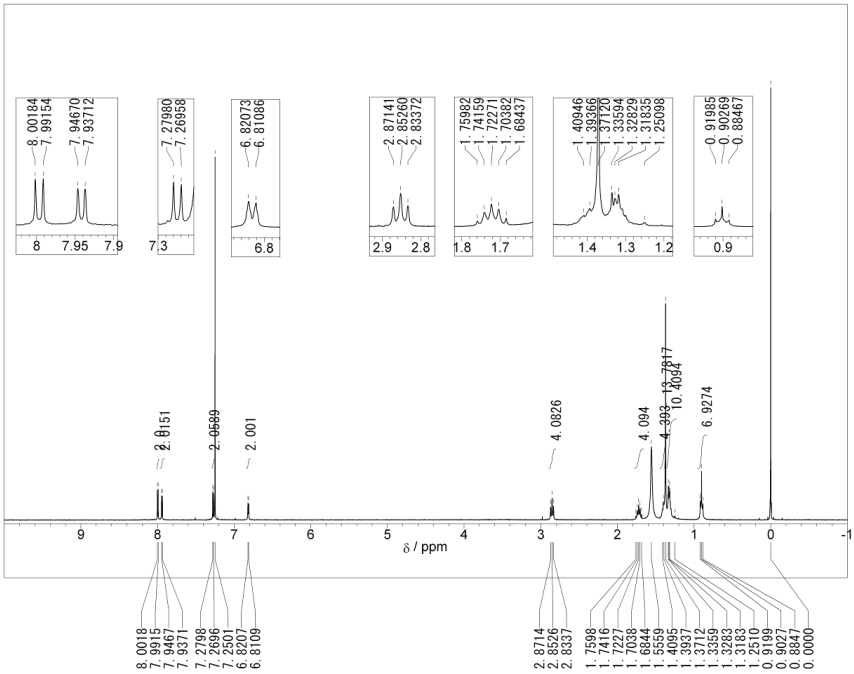
^{1}H NMR spectrum of **$(TC_bT)_4$**



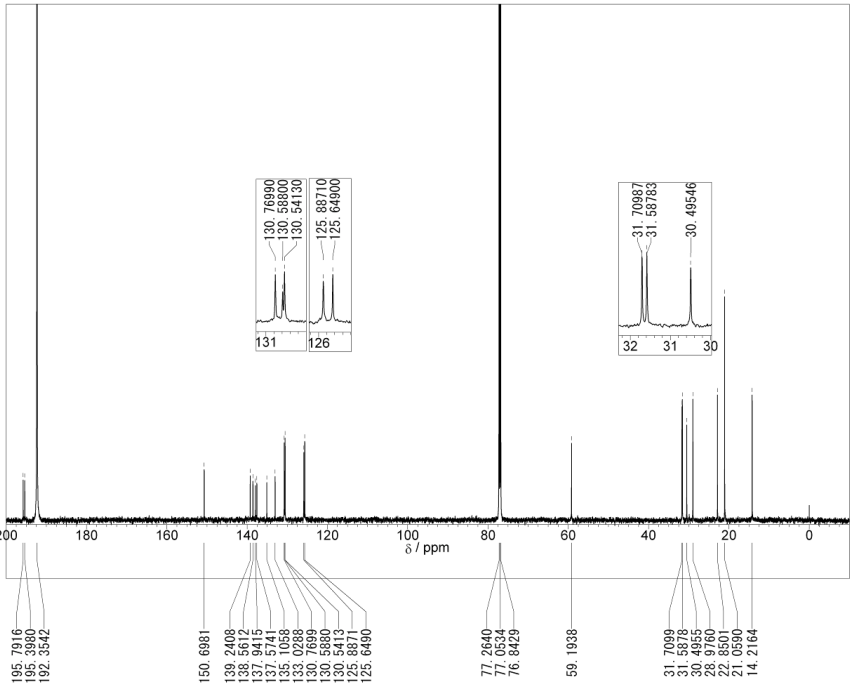
^{13}C NMR spectrum of **$(TC_bT)_4$**



^{1}H NMR spectrum of **h(TC$_m$T)$_2$h**

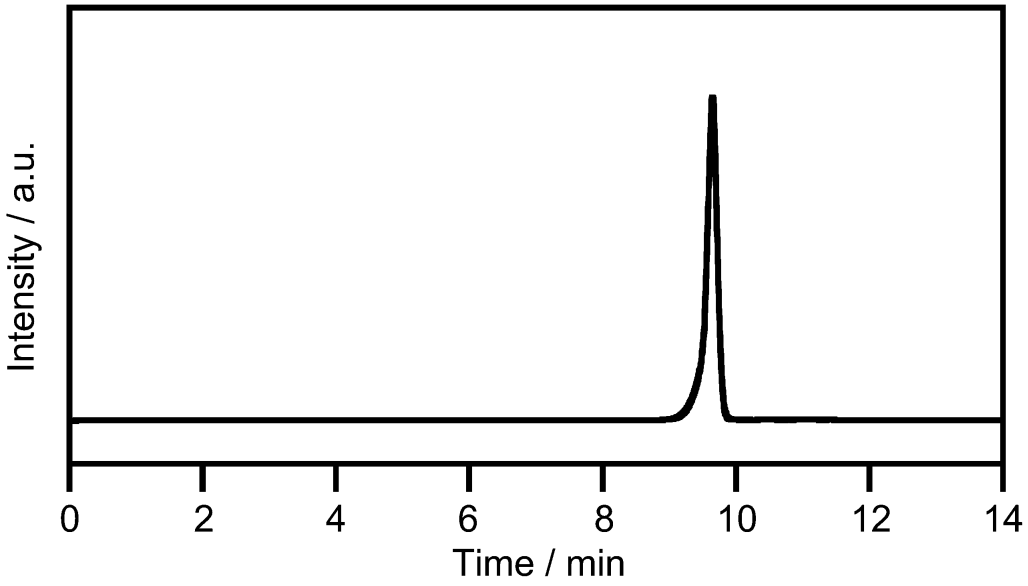


^{13}C NMR spectrum of **h(TC$_m$T)$_2$h**

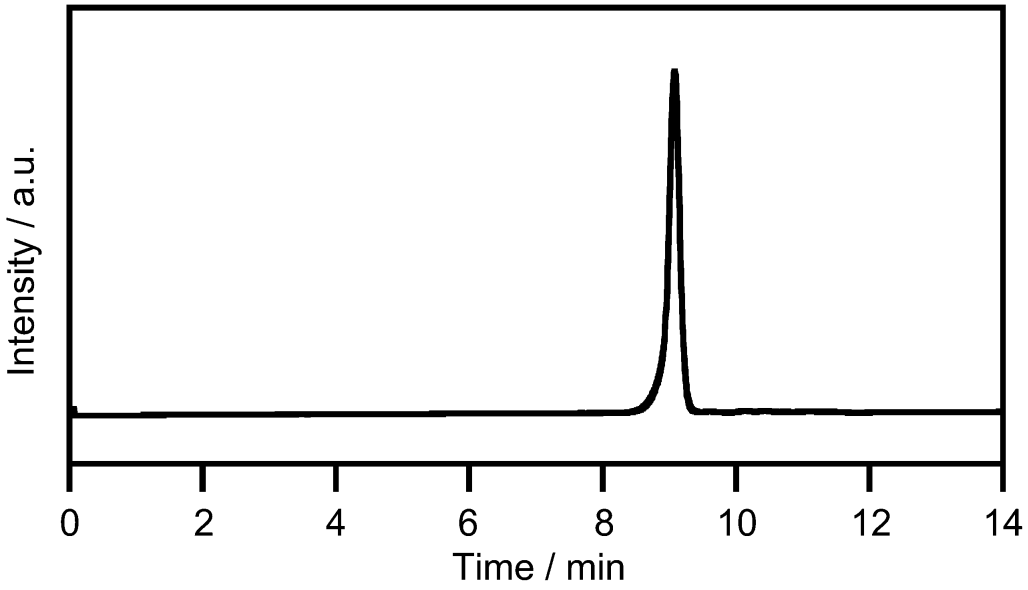


GPC Charts

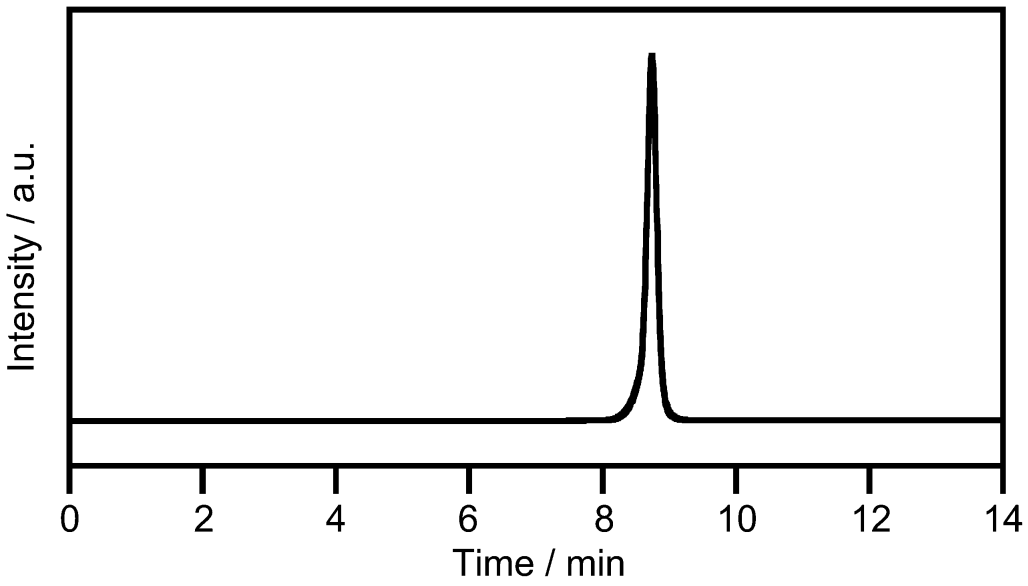
GPC chart of **$(TC_bT)_1$**



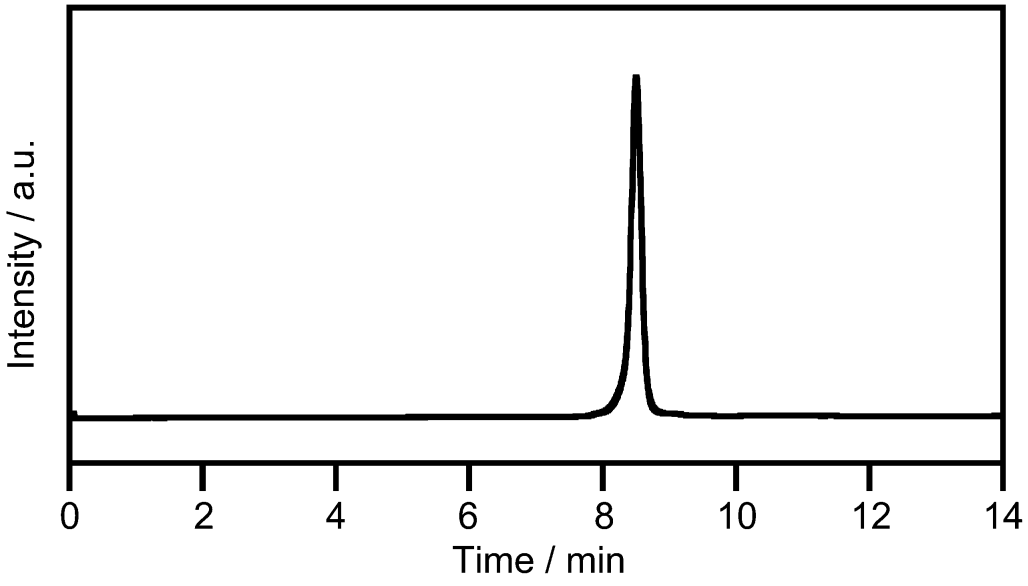
GPC chart of **$(TC_bT)_2$**



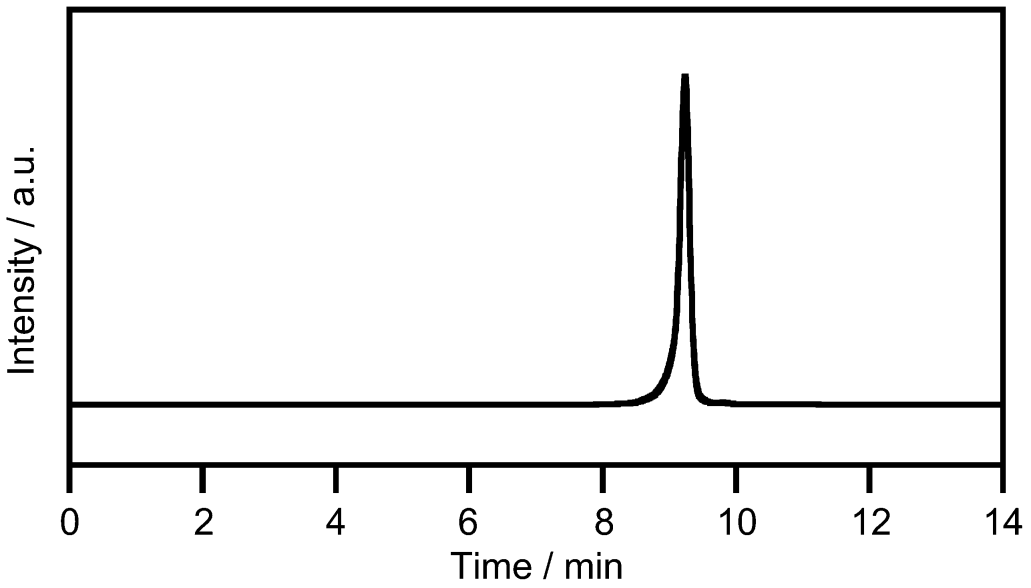
GPC chart of **$(TC_bT)_3$**



GPC chart of **$(TC_bT)_4$**



GPC chart of **h(TC$_m$T)$_2$h**



Computational Details

All calculations were conducted using Gaussian 09 program. The geometry was optimized with the restricted Becke Hybrid (B3LYP) at 6-31 G(d, p) level.

Optimized structure of **$(TC_bT)_2$** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.951581	0.046880	-1.937077
2	6	0	-7.776435	0.052368	-0.633940
3	6	0	-6.836555	0.014366	0.497091
4	6	0	-5.491763	-0.016379	0.011891
5	6	0	-5.487613	-0.015549	-1.457912
6	6	0	-6.956622	0.009529	1.876777
7	16	0	-5.332263	-0.029606	2.569813
8	6	0	-4.519782	-0.038761	1.000044
9	6	0	-8.091215	0.027680	2.767843
10	6	0	-3.082218	-0.057983	0.961639
11	6	0	-7.308112	-1.181479	-2.826091
12	6	0	-7.213636	1.344455	-2.761477
13	6	0	-6.890076	2.652038	-2.064999
14	6	0	-7.133458	-2.542824	-2.181405
15	6	0	-5.606504	3.209592	-2.170980
16	6	0	-5.284417	4.413479	-1.540913
17	6	0	-6.291116	5.055091	-0.796791
18	6	0	-7.581914	4.534532	-0.670060
19	6	0	-8.060214	-4.408815	-0.906179
20	6	0	-6.816470	-5.048927	-1.003579
21	6	0	-5.726978	-4.474544	-1.674152
22	6	0	-5.909733	-3.215523	-2.261106
23	6	0	-3.885014	5.051911	-1.637239
24	6	0	-8.686595	5.235277	0.144451

25	6	0	-4.359460	-5.176521	-1.788982
26	6	0	-9.264400	-5.039918	-0.179597
27	8	0	-8.997532	0.089199	-0.592794
28	8	0	-4.519702	-0.058086	-2.204710
29	6	0	-7.861374	3.319806	-1.318728
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31	16	0	-9.765072	0.073184	2.221855
32	6	0	-10.338534	0.066909	3.850698
33	6	0	-9.319884	0.032172	4.768438
34	6	0	-8.045655	0.009898	4.153865
35	6	0	-2.229765	-0.059565	2.059076
36	6	0	-0.865196	-0.076750	1.726225
37	6	0	-0.635699	-0.088580	0.358821
38	16	0	-2.146182	-0.076314	-0.529289
39	1	0	-11.403287	0.089528	4.039849
40	6	0	6.945993	0.101736	1.952721
41	6	0	5.480533	0.052673	1.475882
42	6	0	5.483945	-0.032085	0.008502
43	6	0	6.828913	-0.043507	-0.477264
44	6	0	7.769666	0.049781	0.649987
45	6	0	4.511564	-0.107514	-0.976815
46	16	0	5.323938	-0.201398	-2.543851
47	6	0	6.948685	-0.136296	-1.853805
48	6	0	3.073864	-0.117879	-0.938224
49	6	0	8.083296	-0.192610	-2.743594
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52	6	0	7.077102	-2.485548	2.241623
53	6	0	6.955376	2.706377	2.016067
54	6	0	8.129815	-3.100418	1.546298
55	6	0	7.971709	-4.353517	0.950809
56	6	0	6.721210	-4.986052	1.074119
57	6	0	5.650866	-4.410349	1.763886

58	6	0	5.413769	4.511285	1.438865
59	6	0	6.434569	5.092081	0.672799
60	6	0	7.708849	4.517467	0.560323
61	6	0	7.948718	3.318713	1.244927
62	6	0	9.105127	-5.051464	0.174318
63	6	0	4.282729	-5.104453	1.909054
64	6	0	8.833650	5.151522	-0.281542
65	6	0	4.012524	5.139955	1.568358
66	8	0	4.512529	0.074915	2.223394
67	8	0	8.990670	0.085568	0.605864
68	6	0	5.853401	-3.147183	2.345099
69	6	0	5.698305	3.312628	2.106100
70	16	0	2.137392	-0.052432	0.550499
71	6	0	0.627418	-0.109612	-0.335891
72	6	0	0.857127	-0.171822	-1.702011
73	6	0	2.221771	-0.176502	-2.034597
74	6	0	8.037052	-0.306135	-4.124993
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77	16	0	9.758247	-0.131027	-2.201324
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79	1	0	-6.682526	-1.113890	-3.722331
80	1	0	-8.349374	-1.053071	-3.139529
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82	1	0	-8.271164	1.327330	-3.045154
83	1	0	-4.864532	2.679750	-2.756501
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86	1	0	-5.091921	-2.738836	-2.793220
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91	6	0	-9.902323	5.521909	-0.768346
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104	1	0	-0.069931	-0.083322	2.462801
105	1	0	8.291986	1.370644	3.040814
106	1	0	6.638060	1.363843	3.663426
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167	1	0	-9.824140	-6.826942	0.914978
168	1	0	-8.133141	-6.376060	1.148569
169	1	0	-8.649536	-7.142304	-0.365743
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175	1	0	-4.422320	6.401193	-3.278689
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177	1	0	-3.278317	4.114159	-3.528473
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199	1	0	3.138531	-3.227109	1.759514
200	1	0	10.215999	-6.930132	0.277573
201	1	0	8.540772	-7.081994	0.820689
202	1	0	9.734443	-6.298420	1.862687

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