Supporting Information

Dinaphtho[2,1-*b*:1′,2′-*d*]thiophenes as High Refractive Index Materials Exploiting the Potential Characteristics of "Dynamic Thiahelicenes"

Yoko Nambu,*[a] Yoko Yoshitake,[a] Shohan Yanagi,[b] Kenji Mineyama,[c] Keisuke Tsurui,[c] Shigeki Kuwata,[a] Toshikazu Takata,[a,#] Tadatomi Nishikubo[d] and Ken Ishikawa[a]

[a]*School of Materials and Chemical Technology, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

[b]*Advanced Materials Development Sector, Tokyo Metropolitan Industrial Technology Research Institute, Aomi, Koto-ku, Tokyo 135-0064, Japan*

[c]*Wakayama Research Institute, Sugai Chemical Co., Uzu, Wakayama, Wakayama 641-0043, Japan*

[d]*Department of Material and Life Chemistry, Kanagawa University,Deceased Dec. 26, 2011.*

Table of Contents

1. DFT Calculations of Polarizability

a. **DNT**

---

uwb97xd/6-311++g(2d,2p) geom=connectivity polar

1/38=1,57=2,172=1/1;

2/12=2,17=6,18=5,40=1/2;

3/5=4,6=6,7=1212,11=2,25=1,30=1,74=-58,116=2/1,2,3;

4//1;

5/5=2,38=5,98=1/2;

8/6=4,10=90,11=11/1;

10/6=1,13=10/2;

6/7=2,8=2,9=2,10=2,28=1/1;

99/5=1,9=1/99;

Electric dipole moment (input orientation):

(Debye = 10**-18 statcoulomb cm , SI units = C m)

(au) (Debye) (10**-30 SI)

Tot 0.569710D+00 0.144806D+01 0.483020D+01

x 0.220859D+00 0.561368D+00 0.187252D+01

y -0.520768D+00 -0.132366D+01 -0.441525D+01

z 0.677609D-01 0.172231D+00 0.574501D+00

Dipole polarizability, Alpha (input orientation).

(esu units = cm**3 , SI units = C**2 m**2 J**-1)

Alpha(0;0):

	(au)	(10**-24 esu)	(10**-40 SI)
iso	0.261602D+03	0.387654D+02	0.431323D+02
aniso	0.194361D+03	0.288013D+02	0.320457D+02

xx	0.342932D+03	0.508172D+02	0.565418D+02
yx	0.765069D+00	0.113372D+00	0.126143D+00
yy	0.307190D+03	0.455208D+02	0.506487D+02
zx	0.138158D+02	0.204729D+01	0.227792D+01
zy	-0.289028D+00	-0.428295D-01	-0.476543D-01
zz	0.134684D+03	0.199581D+02	0.222063D+02

b. DBT

 # wb97xd/6-311++g(2d,2p) geom=connectivity polar

1/38=1,57=2,172=1/1;

2/12=2,17=6,18=5,40=1/2;

3/5=4,6=6,7=1212,11=2,25=1,30=1,74=-58/1,2,3;

4//1;

5/5=2,38=5,98=1/2;

8/6=4,10=90,11=11/1;

10/6=1,13=10/2;

6/7=2,8=2,9=2,10=2,28=1/1;

99/5=1,9=1/99;

Electric dipole moment (dipole orientation):

(Debye = 10**-18 statcoulomb cm , SI units = C m)

	(au)	(Debye)	(10**-30 SI)
Tot	0.324750D+00	0.825433D+00	0.275335D+01
x	0.000000D+00	0.000000D+00	0.000000D+00
y	0.000000D+00	0.000000D+00	0.000000D+00
z	0.324750D+00	0.825433D+00	0.275335D+01

Dipole polarizability, Alpha (dipole orientation).

(esu units = cm**3 , SI units = C**2 m**2 J**-1)

Alpha(0;0):

	(au)	(10**-24 esu)	(10**-40 SI)
iso	0.158938D+03	0.235522D+02	0.262054D+02
aniso	0.127726D+03	0.189271D+02	0.210592D+02
xx	0.230031D+03	0.340871D+02	0.379270D+02
yx	-0.685529D-02	-0.101585D-02	-0.113029D-02
yy	0.828042D+02	0.122703D+02	0.136526D+02
zx	-0.374351D-03	-0.554731D-04	-0.617222D-04
zy	0.446880D-04	0.662209D-05	0.736806D-05
zz	0.163979D+03	0.242992D+02	0.270365D+02

2. Density Measurement

a. DNT

Sample Mass: 0.9919 g
Temperature: 27.0 °C
Number of Purges: 10
Cell Volume: 11.3110 cm3

Equilibration Rate: 0.0345 kPag/min
Expansion Volume: 8.4328 cm3

Cycle#	Volume cm3	Deviation cm3	Density g/cm3	Deviation g/cm3	Elapsed Time	Temperature °C
1	0.7157	0.0003	1.3859	-0.0005	0:10:27	26.9
2	0.7158	0.0004	1.3858	-0.0007	0:13:17	27.0
3	0.7152	-0.0002	1.3869	0.0004	0:16:04	27.0
4	0.7141	-0.0014	1.3891	0.0026	0:19:15	27.0
5	0.7164	0.0010	1.3846	-0.0018	0:22:04	27.0

Average Volume: 0.7154 cm3
Average Density: 1.3865 g/cm3

Standard Deviation: 0.0008 cm3
Standard Deviation: 0.0015 g/cm3

Sample Mass: 0.9919 g
Temperature: 27.1 °C
Number of Purges: 10
Cell Volume: 11.3110 cm3

Equilibration Rate: 0.0345 kPag/min
Expansion Volume: 8.4328 cm3

Cycle#	Volume cm3	Deviation cm3	Density g/cm3	Deviation g/cm3	Elapsed Time	Temperature °C
1	0.7167	-0.0002	1.3840	0.0004	0:09:18	27.0
2	0.7174	0.0005	1.3826	-0.0010	0:12:07	27.0
3	0.7176	0.0007	1.3823	-0.0014	0:15:21	27.0
4	0.7153	-0.0016	1.3868	0.0032	0:17:51	27.1
5	0.7175	0.0006	1.3824	-0.0012	0:20:56	27.1

Average Volume: 0.7169 cm3
Average Density: 1.3836 g/cm3

Standard Deviation: 0.0009 cm3
Standard Deviation: 0.0017 g/cm3

Sample Mass: 0.9919 g
Temperature: 27.1 °C
Number of Purges: 10
Cell Volume: 11.3110 cm3

Equilibration Rate: 0.0345 kPag/min
Expansion Volume: 8.4328 cm3

Cycle#	Volume cm3	Deviation cm3	Density g/cm3	Deviation g/cm3	Elapsed Time	Temperature °C
1	0.7142	-0.0037	1.3887	0.0072	0:10:33	27.1
2	0.7162	-0.0018	1.3850	0.0034	0:12:55	27.0
3	0.7210	0.0030	1.3758	-0.0058	0:16:11	27.1
4	0.7190	0.0011	1.3795	-0.0021	0:19:23	27.1
5	0.7193	0.0014	1.3790	-0.0026	0:22:12	27.1

Average Volume: 0.7179 cm3
Average Density: 1.3816 g/cm3

Standard Deviation: 0.0024 cm3
Standard Deviation: 0.0046 g/cm3

b. DBT

Sample Mass: 0.8757 g
Temperature: 26.8 °C
Number of Purges: 10
Cell Volume: 11.3110 cm3

Equilibration Rate: 0.0345 kPag/min
Expansion Volume: 8.4328 cm3

Cycle#	Volume cm3	Deviation cm3	Density g/cm3	Deviation g/cm3	Elapsed Time	Temperature °C
1	0.6628	0.0053	1.3213	-0.0106	0:09:21	26.7
2	0.6564	-0.0011	1.3342	0.0023	0:12:22	26.7
3	0.6563	-0.0012	1.3343	0.0024	0:15:49	26.7
4	0.6557	-0.0018	1.3355	0.0036	0:18:12	26.8
5	0.6563	-0.0012	1.3344	0.0024	0:21:08	26.8

Average Volume: 0.6575 cm3
Average Density: 1.3319 g/cm3

Standard Deviation: 0.0027 cm3
Standard Deviation: 0.0053 g/cm3

Sample Mass: 0.8757 g
Temperature: 26.9 °C
Number of Purges: 10
Cell Volume: 11.3110 cm3

Equilibration Rate: 0.0345 kPag/min
Expansion Volume: 8.4328 cm3

Cycle#	Volume cm3	Deviation cm3	Density g/cm3	Deviation g/cm3	Elapsed Time	Temperature °C
1	0.6567	-0.0004	1.3334	0.0008	0:09:35	26.8
2	0.6572	0.0001	1.3325	-0.0002	0:12:23	26.9
3	0.6580	0.0009	1.3309	-0.0017	0:15:22	26.9
4	0.6576	0.0004	1.3317	-0.0009	0:18:37	26.9
5	0.6562	-0.0010	1.3346	0.0020	0:21:54	27.0

Average Volume: 0.6571 cm3
Average Density: 1.3326 g/cm3

Standard Deviation: 0.0006 cm3
Standard Deviation: 0.0013 g/cm3

Sample Mass: 0.8757 g
Temperature: 27.0 °C
Number of Purges: 10
Cell Volume: 11.3110 cm3

Equilibration Rate: 0.0345 kPag/min
Expansion Volume: 8.4328 cm3

Cycle#	Volume cm3	Deviation cm3	Density g/cm3	Deviation g/cm3	Elapsed Time	Temperature °C
1	0.6583	0.0001	1.3302	-0.0002	0:10:13	26.9
2	0.6584	0.0002	1.3299	-0.0005	0:13:08	26.9
3	0.6585	0.0002	1.3299	-0.0005	0:15:55	26.9
4	0.6576	-0.0006	1.3317	0.0013	0:18:32	26.9
5	0.6583	0.0001	1.3303	-0.0001	0:21:33	26.9

Average Volume: 0.6582 cm3
Average Density: 1.3304 g/cm3

Standard Deviation: 0.0003 cm3
Standard Deviation: 0.0006 g/cm3

3. X Ray Crystallographic Analysis

Crystallographic data of **DNT** and **DBT** have been deposited with the Cambridge Crystallographic Data Centre as CCDC No. 979346 (**DNT)** and CCDC No. 979347 (**DBT)**. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or via https://www.ccdc.cam.ac.uk/structures/).

a. Data Collection of DNT

A colorless prism crystal of $C_{20}H_{12}S$ having approximate dimensions of 0.340 x 0.180 x 0.070 mm was mounted on a glass fiber. All measurements were made on a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo-Kα radiation. The crystal-to-detector distance was 45.03 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

$$a = 21.334(12)\ \text{Å},\ b = 8.374(5)\ \text{Å},\ c = 7.256(4)\ \text{Å},\ V = 1296.3(13)\ \text{Å}^3$$

For $Z = 4$ and $F.W. = 284.37$, the calculated density is 1.457 g/cm^3.

The reflection conditions of: $0kl$: $k = 2n$, $h0l$: $l = 2n$, $hk0$: $h+k = 2n$

uniquely determine the space group to be: *Pbcn* (#60)

The data were collected at a temperature of -179 + 1°C to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was done using w oscillations from -110.0 to 70.0° in 0.5° steps. The exposure rate was 6.0 [sec./°]. The detector swing angle was -19.91°. A second sweep was performed using ω oscillations from -110.0 to 70.0° in 0.5° steps. The exposure rate was 6.0 [sec./°]. The detector swing angle was -19.91°. The crystal-to-detector distance was 45.03 mm. Readout was performed in the 0.141 mm pixel mode.

b. Data Reduction of DNT

Of the 8166 reflections that were collected, 1443 were unique ($R_{int} = 0.0497$); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).[1]

The linear absorption coefficient, ω, for Mo-Kα radiation is 2.373 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.768 to 0.984. The data were corrected for Lorentz and polarization effects.

c. Structure Solution and Refinement of DNT

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 1443 observed reflections and 96 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$R_1 = \Sigma\ (|F_o| - |F_c|)/\ \Sigma\ |F_o| = 0.0497$

$wR_2 = [\ \Sigma\ (w\ (F_o^2 - F_c^2)^2\ )/\ \Sigma\ w(F_o^2)^2]^{1/2} = 0.1382$

The goodness of fit[4] was 1.09. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.76 and -0.31 e/Å^3, respectively.

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4[5]. Anomalous dispersion effects were included in F_{calc}[6]; the values for $\Delta f'$ and Df''were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell.[8] All calculations were performed using the CrystalStructure[9] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[10]

d. Data Collection of DBT

A colorless prism crystal of $C_{12}H_8S$ having approximate dimensions of 0.230 x 0.210 x 0.150 mm was mounted on a glass fiber. All measurements were made on a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo-Kα radiation.

The crystal-to-detector distance was 45.00 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 8.560(3) Å, b = 5.963(2) Å, c = 16.980(7) Å, β = 94.392(5)°, V = 864.1(6) Å^3

For Z = 4 and *F.W.* = 184.26, the calculated density is 1.416 g/cm^3. The reflection conditions of:

h0l: $h+l$ = 2n, *0k0*: k = 2n

uniquely determine the space group to be: $P2_1/n$ (#14)

The data were collected at a temperature of -179 ± 1°C to a maximum 2θ value of 54.9°. A total of 720 oscillation images were collected. A sweep of data was done using ω oscillations from -110.0 to 70.0° in 0.50° steps. The exposure rate was 4.0 [sec./°]. The detector swing angle was -19.86°. A second sweep was performed using ω oscillations from -110.0 to 70.0° in 0.5° steps. The exposure rate was 4.0 [sec./°]. The detector swing angle was -19.86°. The crystal-to-detector distance was 45.00 mm. Readout was performed in the 0.141 mm pixel mode.

e. Data Reduction of DBT

Of the 5762 reflections that were collected, 1919 were unique (R_{int} = 0.0698); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).[1]

The linear absorption coefficient, ω, for Mo-Kα radiation is 3.123 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.844 to 0.954. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction[2] was applied (coefficient = 14.708000).

f. Structure Solution and Refinement of DBT

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on

1919 observed reflections and 96 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$R_1 = \Sigma\ (|F_o| - |F_c|)/\Sigma\ |F_o| = 0.0489$

$wR_2 = [\ \Sigma\ (w\ (F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2} = 0.1317$

The goodness of fit[4] was 1.13. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.76 and -0.31 e /Å^3, respectively.

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4[5]. Anomalous dispersion effects were included in F_{calc}[6]; the values for $\Delta f'$ and $\Delta f''$were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell.[8] All calculations were performed using the CrystalStructure[9] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[10]

References of X Ray Crystallographic Analysis

1. CrystalClear: Data Collection and Processing Software, Rigaku Corporation, 1998-2015. Tokyo, Japan.

2. SIR92: A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst*. 1993, **26**, 343-350.

3. Least Squares function minimized: (SHELXL Version 2014/7)

   $\Sigma w(Fo^2 - Fc^2)^2$ where: w = Least Squares weights.

4. Goodness of fit is defined as:

   $[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$ where: N_o = number of observation, N_v = number of variables

5. *International Tables for Crystallography*,.*C*. (Ed.: A.J.C. Wilson), Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, 1992, 572.

6. J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

7. D. C. Creagh, W. J. McAuley in *International Tables for Crystallography*, *C*, (Ed.: A.J.C. Wilson), Kluwer Academic Publishers, Boston, Table 4.2.6.8, 1992, 219-222.

8. D. C. Creagh, J. H. Hubbell in *International Tables for Crystallography*, *C*, (Ed.: A.J.C. Wilson), Kluwer Academic Publishers, Boston, Table 4.2.6.8, 1992, 200-206.

9. CrystalStructure 4.3: *Crystal Structure Analysis Package*, Rigaku Corporation, 2000-2018, Tokyo, Japan.

10. SHELXL Version 2014/7: G. M. Sheldrick, *Acta Cryst*. 2008, **A64**, 112-122.

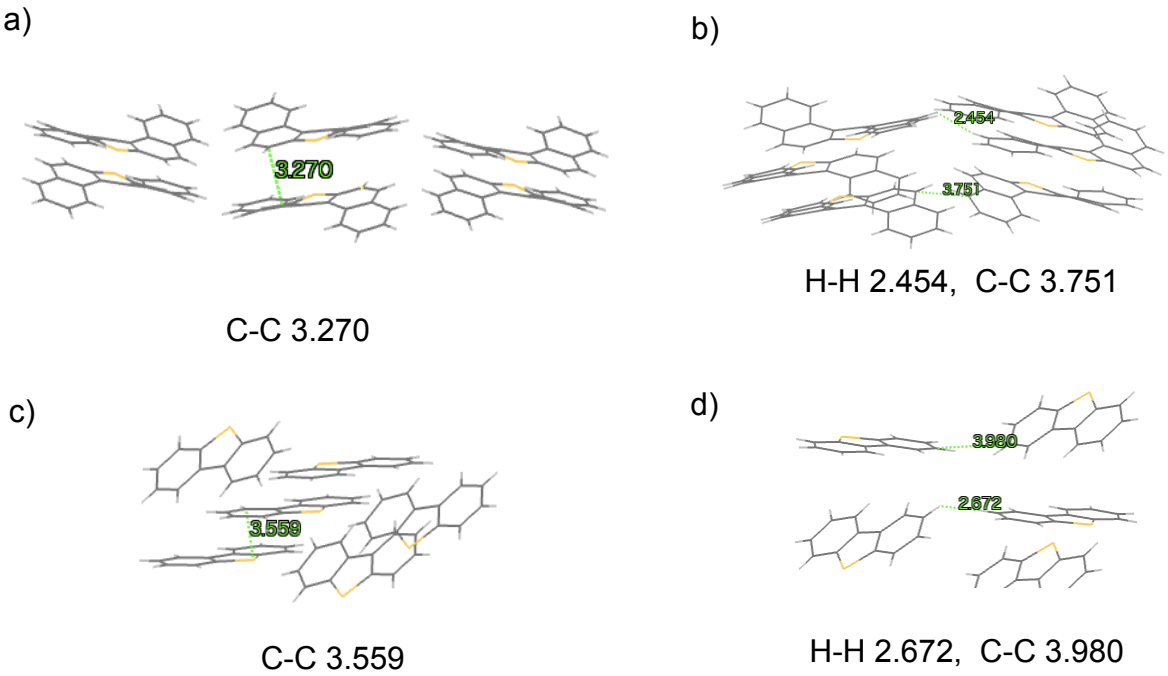
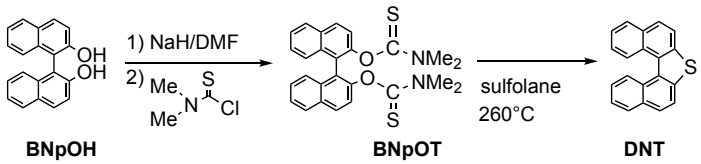


Fig. S1 Comparison of single crystals of **DNT** and **DBT** by the distance (Å) between stacked aromatics of a) **DNT** and c) **BDT**, and by the distance (Å) between neighboring molecules of b) **DNT** and d) **BDT**.

4. Synthetic Procedures

1. Synthesis of dinaphtho[2,1-*b*:1',2'-*d*]thiophene (DNT)



BNpOH BNpOT DNT

To a solution of 1,1'-binaphthol (20.0 g, 69.9 mmol) in DMF (150 mL), was added sodium hydride (55% oil dispersion) (6.7 g, 153.7 mmol) portionwise. The mixture was stirred for 1 h at 0 ^{o}C, and then N, N-dimethylcarbamoyl chloride (purity 95%, 20.0 g 153.7 mmol) was added. The reaction solution was stirred for 1 h at 85 ^{o}C, cooled to room temperature and poured into 1% aqueous KOH (500 mL) with vigorous stirring. The precipitate was collected by filtration, washed with water and dissolved in CH_2Cl_2. The solution was dried over $MgSO_4$, and solvent was removed in vacuo. The crude product was recrystallized from CH_2Cl_2-petrolium ether to obtain **BNpOT** (27.4 g, 85.0%). mp.205.9 − 206.8 ^{o}C (lit. mp, 200 − 209.5 ^{o}C). Next, **BNpOT** (6.0 g, 13.1 mmol) was dissolved in sulfolane (12 mL), heated for 2 h at 260 ^{o}C with vigorous stirring, and cooled to room temperature. The reaction solution was poured into water, and the precipitate was collected by filtration. After drying under reduced pressure the precipitate was dissolved in $CHCl_3$, decolorized over active carbon and recrystallized from $CHCl_3$-*n*-hexane to give **DNT** (2.6 g, 71.0%) as a white powder. m.p. 207.5 − 208.3 ^{o}C (lit.[1] m.p. 208-209 ^{o}C).
^{1}H NMR and ^{13}C NMR spectra were in agreement with the reported data.[2]

References

1. V. N. Gogte, V. S. Palkar and B. D. Tilak, *Tetrahedron Lett.*, 1960, **1**, 30-34.
2. T. Zhang, G. Deng, H. Li, B. Liu, Q. Tan and B. Xu, *Org. Lett.*, 2018, **20**, 5439-5443.

5. ^{1}H and ^{13}C NMR Spectra

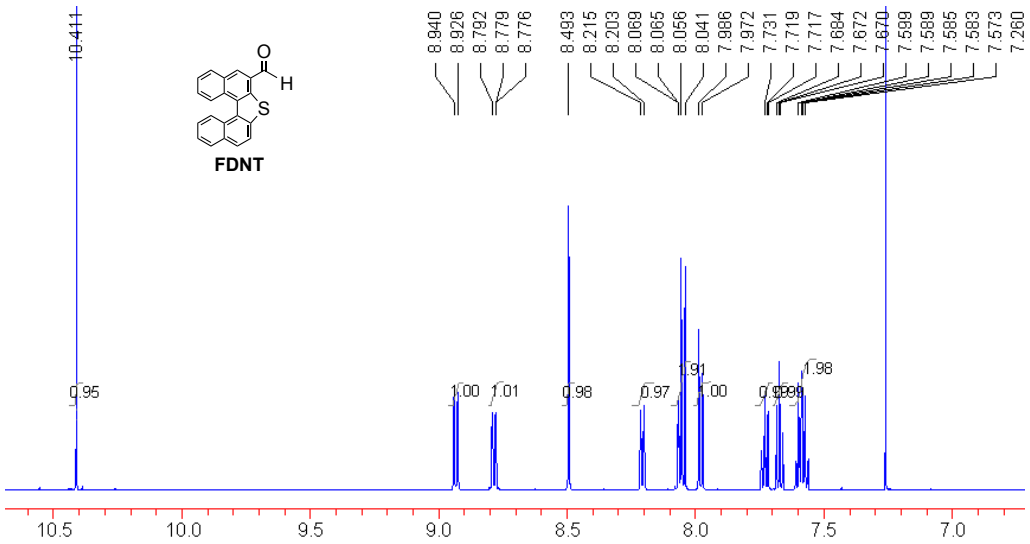


Fig. S2. ^{1}H NMR spectrum of **FDNT** (600 MHz, $CDCl_3$, 298 K, ppm).

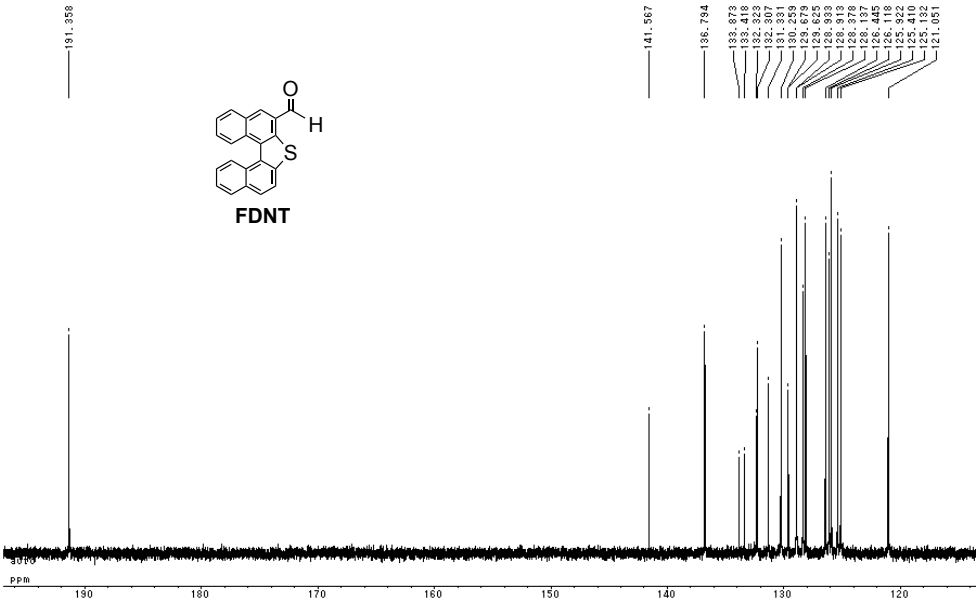


Fig. S3 ^{13}C NMR spectrum of **FDNT** (150 MHz, $CDCl_3$, 298 K, ppm).

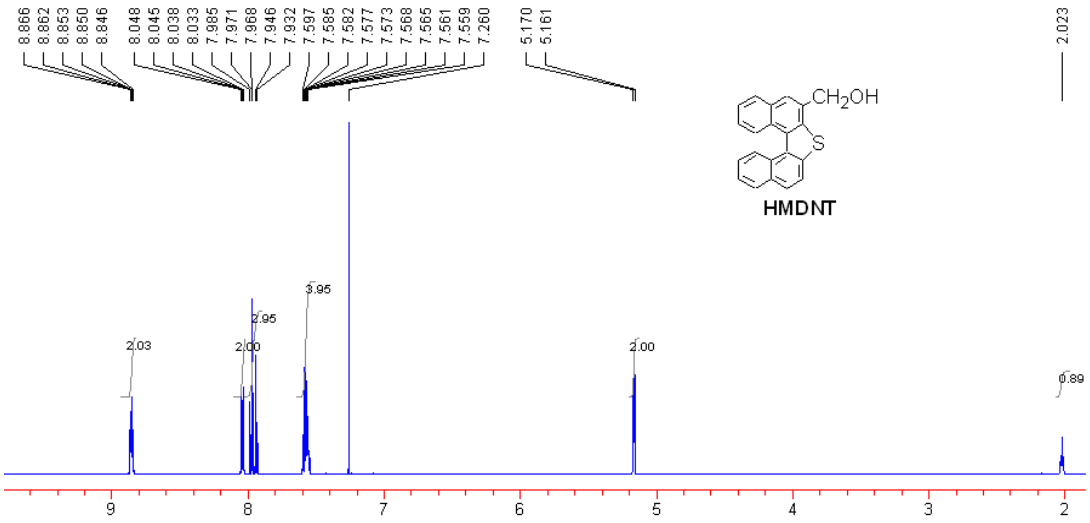


Fig. S4 ^{1}H NMR spectrum of **HMDNT** (600 MHz, $CDCl_3$, 298 K, ppm).

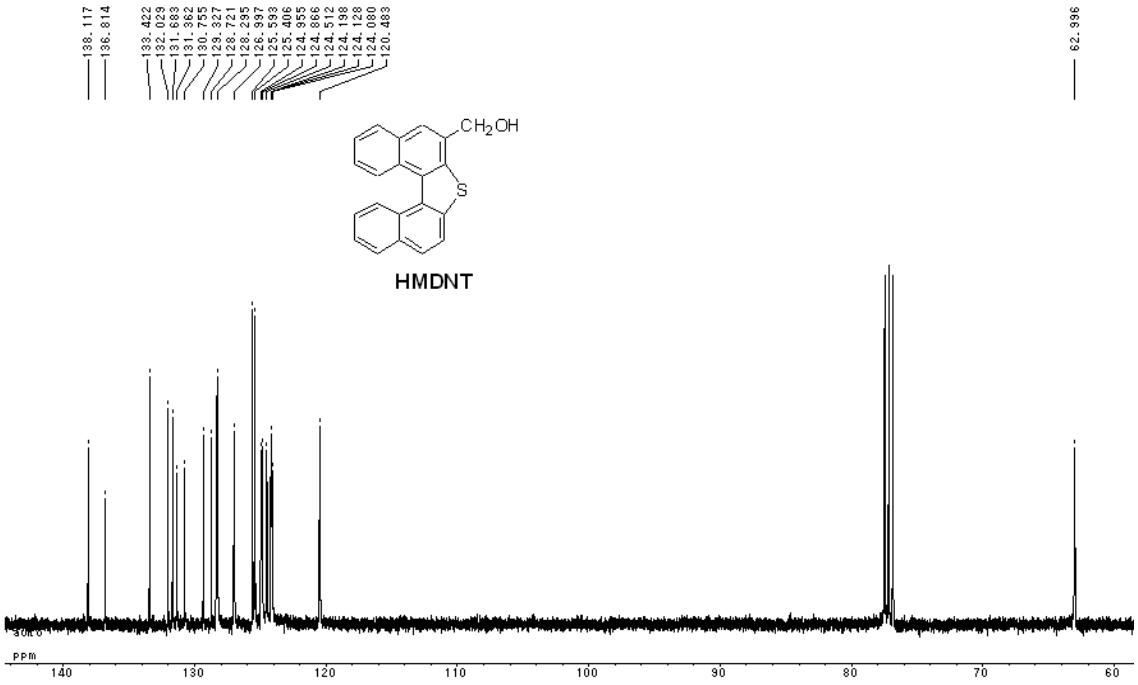


Fig. S5 ^{13}C NMR spectrum of HMDNT (150 MHz, CDCl3, 298 K, ppm).

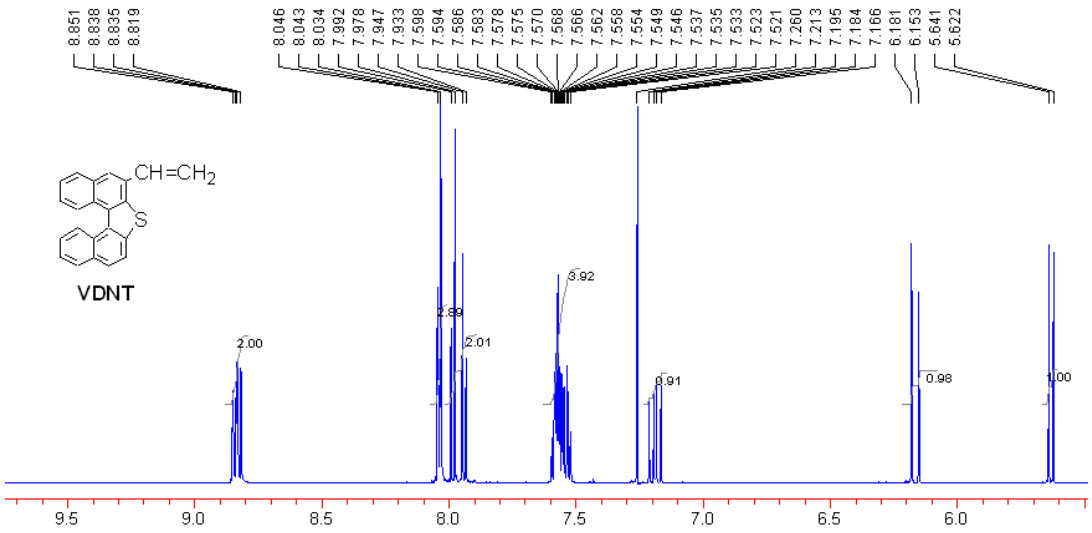


Fig. S6 ^{1}H NMR spectrum of **VDNT** (600 MHz, $CDCl_3$, 298 K, ppm).

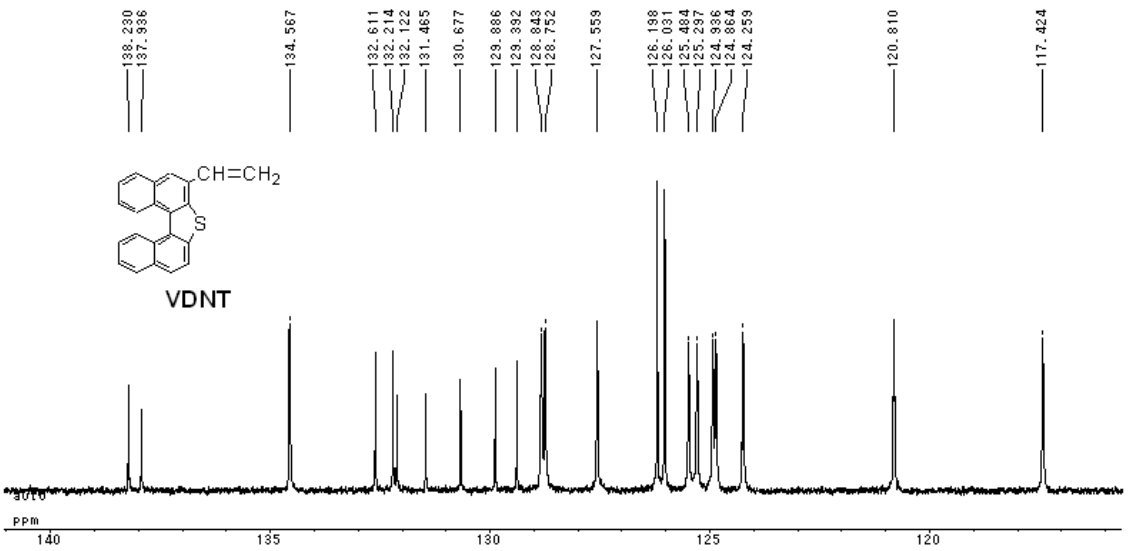


Fig. S7 ^{13}C NMR spectrum of **VDNT** (150 MHz, $CDCl_3$, 298 K. ppm)

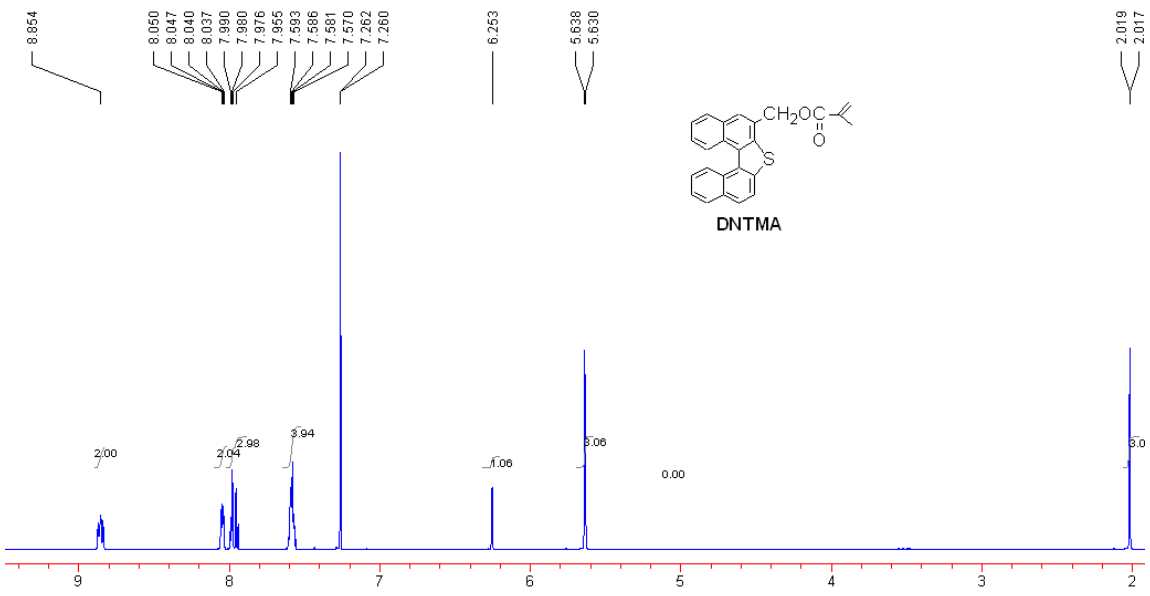


Fig. S8 ^{1}H NMR spectrum of **DNTMA** (600 MHz, $CDCl_3$, 298 K, ppm).

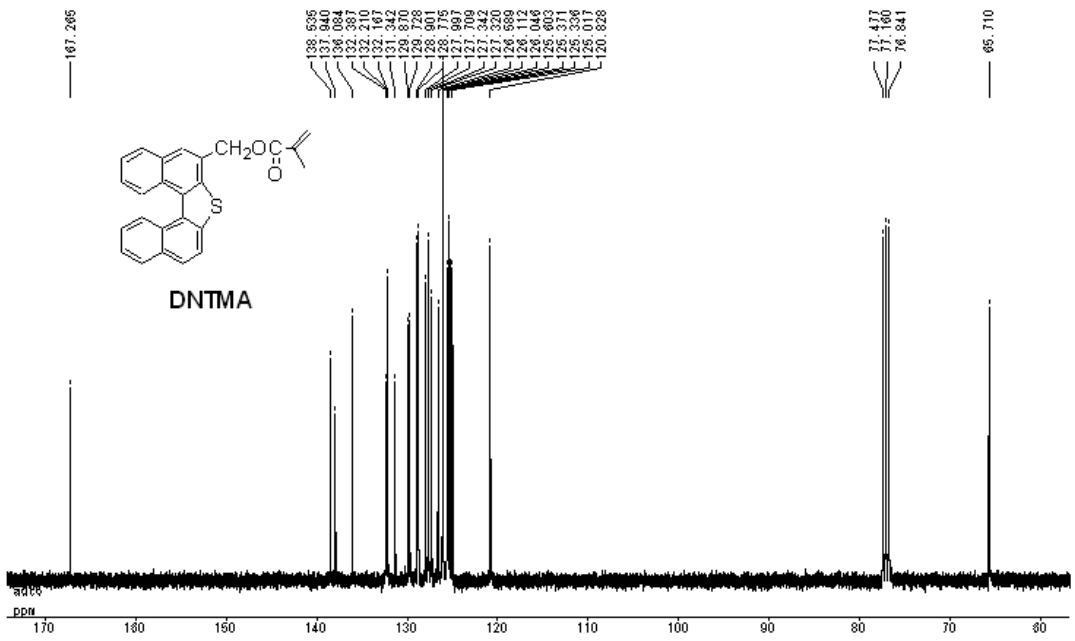


Fig. S9 ^{13}C NMR spectrum of **DNTMA** (150 MHz, $CDCl_3$, 298 K, ppm).

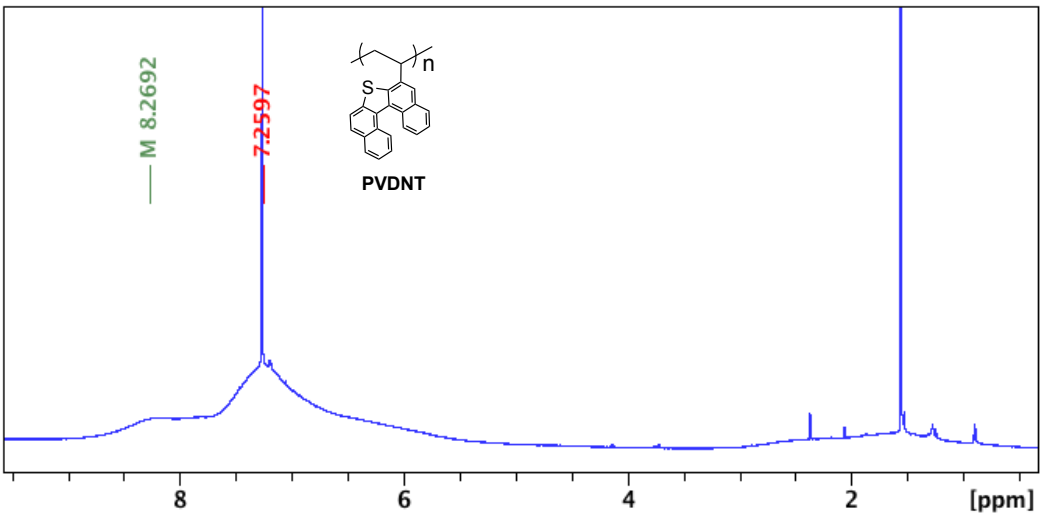


Fig. S10 ^{1}H NMR spectrum of **PVDNT** (500 MHz, $CDCl_3$, 298 K).

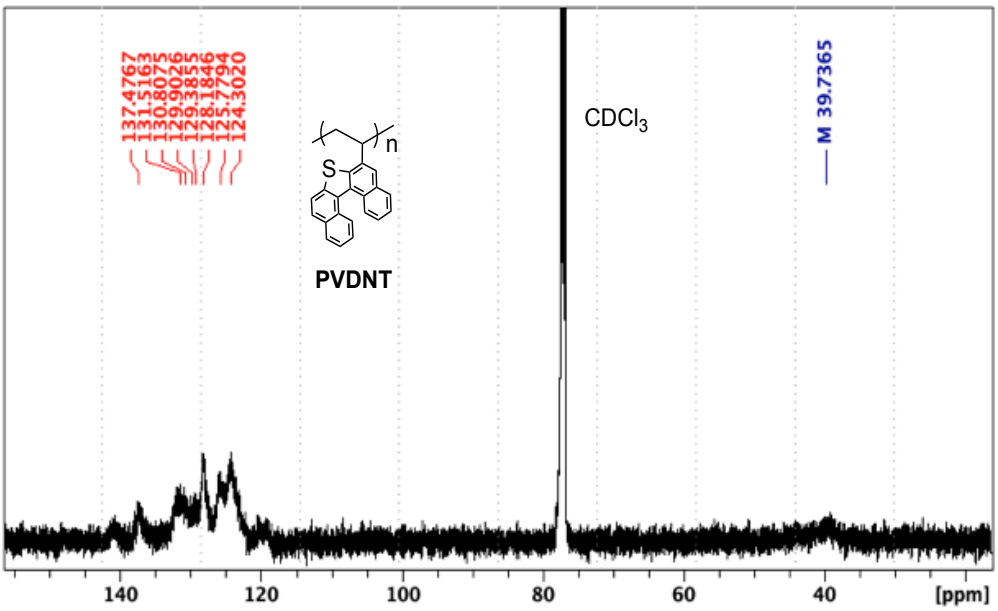


Fig. S11 ^{13}C NMR spectrum of **PVDNT** (125 MHz, $CDCl_3$, 298 K).

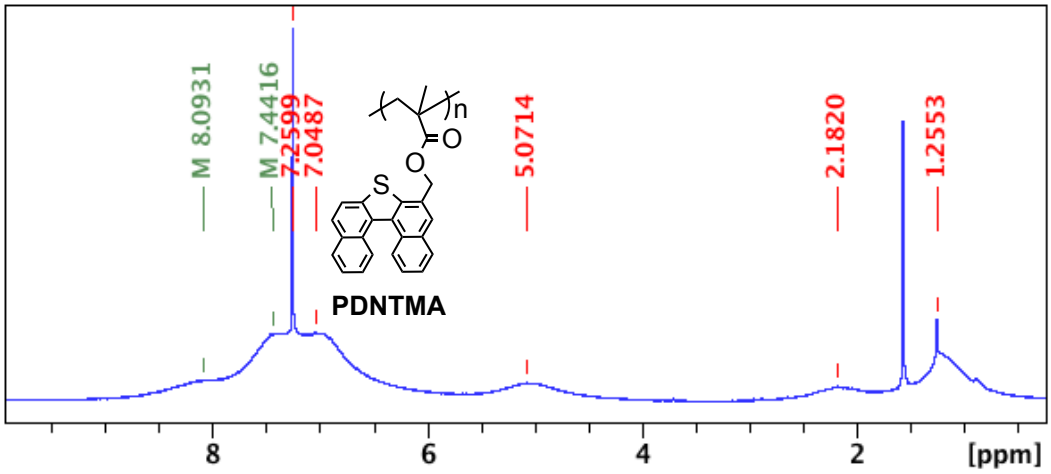


Fig. S12 ^{1}H NMR spectrum of **PDNTMA** (500 MHz, $CDCl_3$, 298 K).

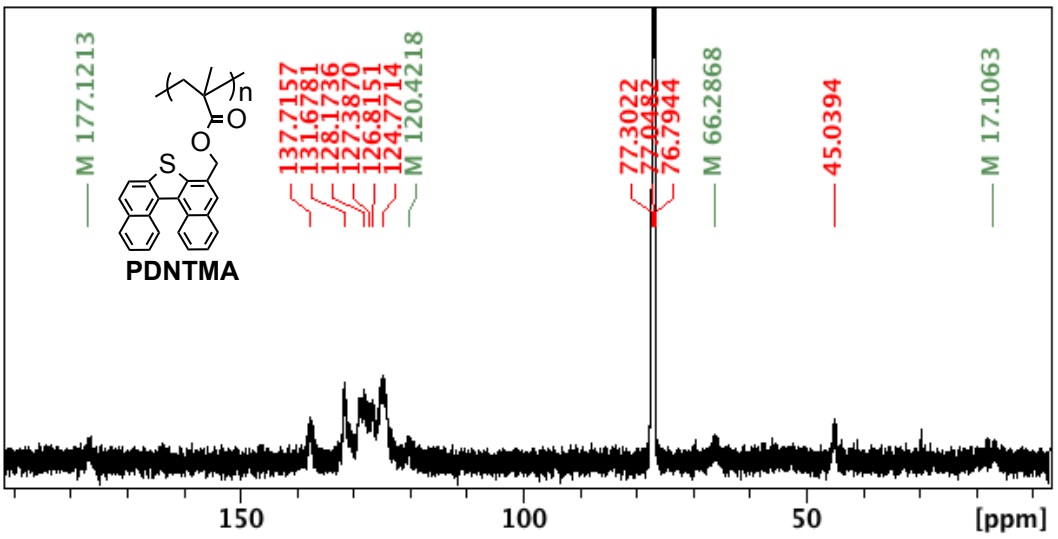


Fig. S13 ^{13}C NMR spectrum of **PDNTMA** (125 MHz, $CDCl_3$, 298 K).

6. DSC Profiles

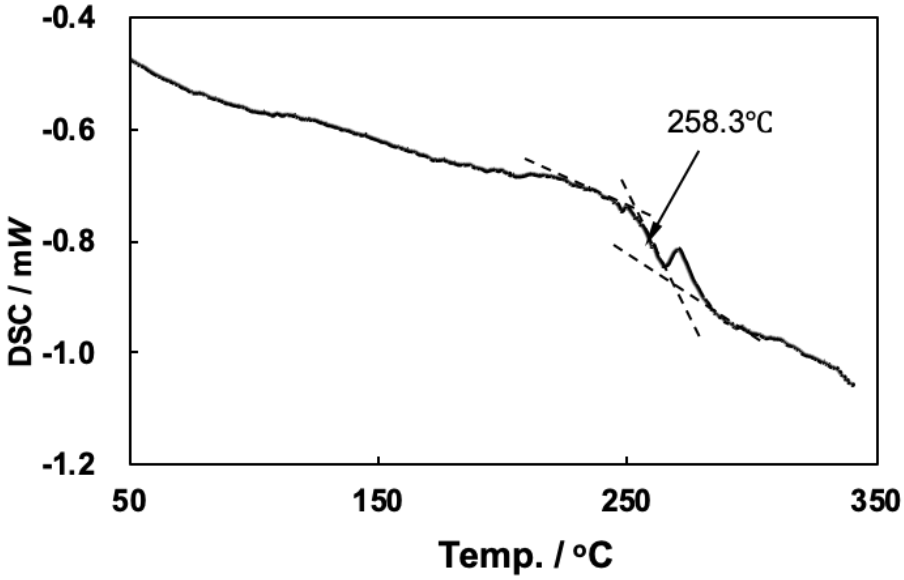


Fig. S14 Differential scanning calorimetric analysis of **PVDNT**.

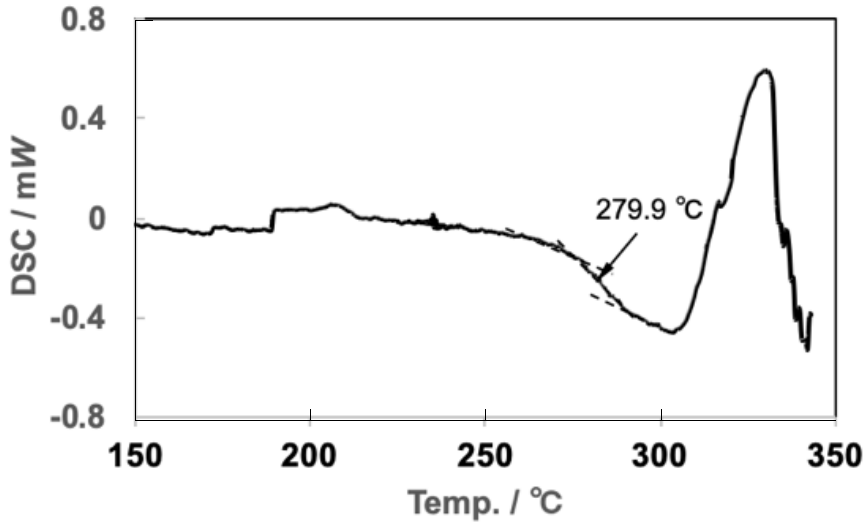


Fig. S15 Differential scanning calorimetric analysis of **PDNTMA**.