Supporting Information

Core-Expanded Naphthalene Diimides Fused with 2-(1,3-Dithiol-2-Ylidene)Malonitrile Groups for High-Performance, Ambient-Stable, Solution-Processed n-Channel Organic Thin Film Transistors

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Contents:

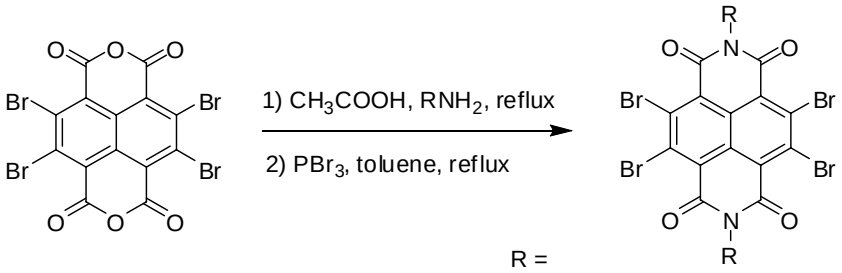
Experimental Section

Materials and General Methods.

Chemicals were purchased from Aldrich, Alfa Aesar and used as received. Solvents and other common reagents were obtained from the Sinopharm Chemical Reagent Co., Ltd. 2,3,6,7-Tetrabromonaphthalene dianhydride (TBNDA),[1] 2-decyl-teradecylamine,[2] 2-octyl-dodecylamine,[3] and sodium 1,1-dicyanoethylene-2,2-dithiolate[4] were synthesized according to the reported procedures. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (100 MHz) spectra were measured in $CDCl_3$ on Varian Mercury (300 MHz or 400 MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra (MALDI-TOF) were carried out on a Voyager-DE STR Mass Spectrometer. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. FT-IR spectra were determined using a Bio-Rad FTS-185 spectrometer. Electronic absorption spectra were measured on a Jasco V570 UV-vis spectrophotometer. TGA measurements were carried out on a TA Q500 instruments under a dry nitrogen flow at a heating rate of 10 °C/min, heating from room temperature to 500°C. DSC analyses were performed on a Perkin Elmer Pyris 1 instruments under a dry N_2 flow at a heating rate of 10 °C/min, heating from room temperature to 300 °C. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a platinum button working electrode of 2 mm diameter, a platinum wire counter electrode, and a SCE reference electrode on a computer-controlled CHI610D instruments. X-ray diffraction (XRD) measurements were carried out in the reflection mode using a 2-kW Rigaku X-ray diffraction system. AFM was recorded on a Nanoscope IIIa atomic force microscopy (AFM) in trapping mode.

Synthetic Details

Synthesis of compounds 3 and 4.



TBNDA

R =

2-decyl-tetracosyl **3**

2-octyl-dodecyl **4**

Scheme S1

Safety precautions should be cautioned for the synthesis of 2,3,6,7-Tetrabromonaphthalene dianhydride (TBNDA).[1].

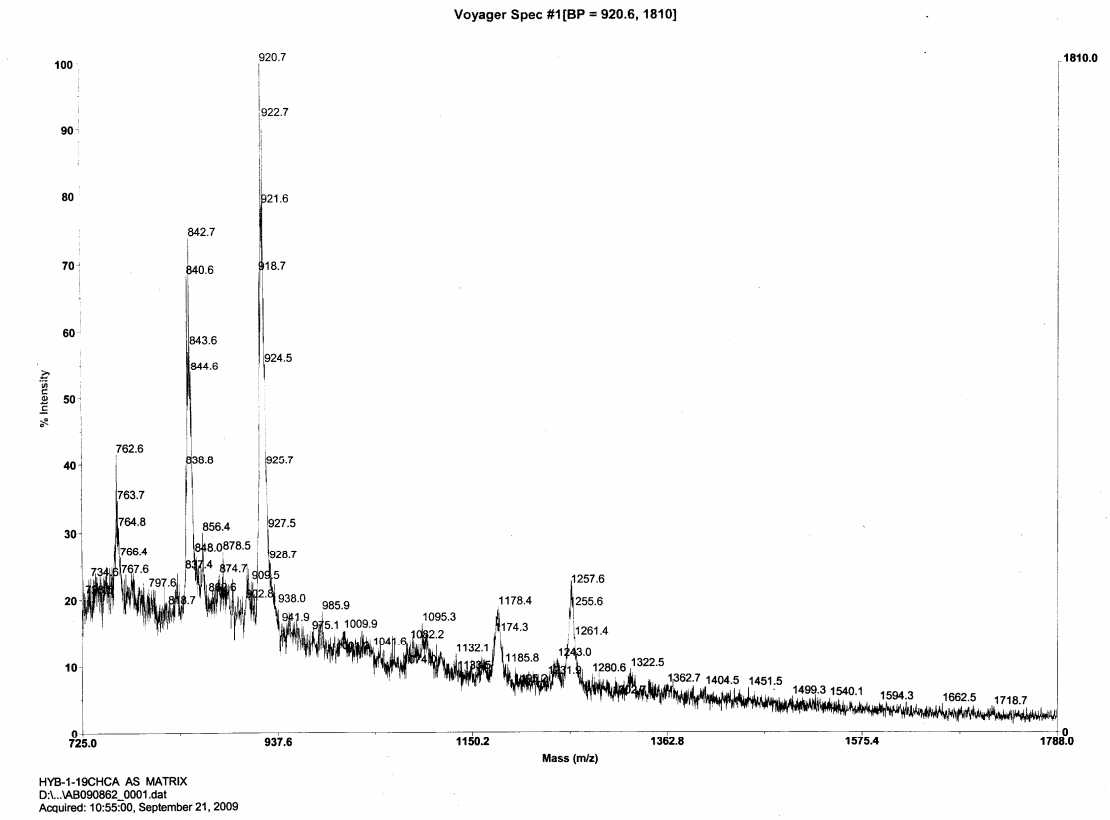
Safety Precautions: During the reaction, the glass water-cooled condenser could be blocked by solid SO_3. To give off bromine hydride, the blocked condenser should be continuously replaced. Plugging of the blocked condenser using flinty tools is forbidden (when the condenser was broken, the water will flow into the boiling oleum, and this is very dangerous).

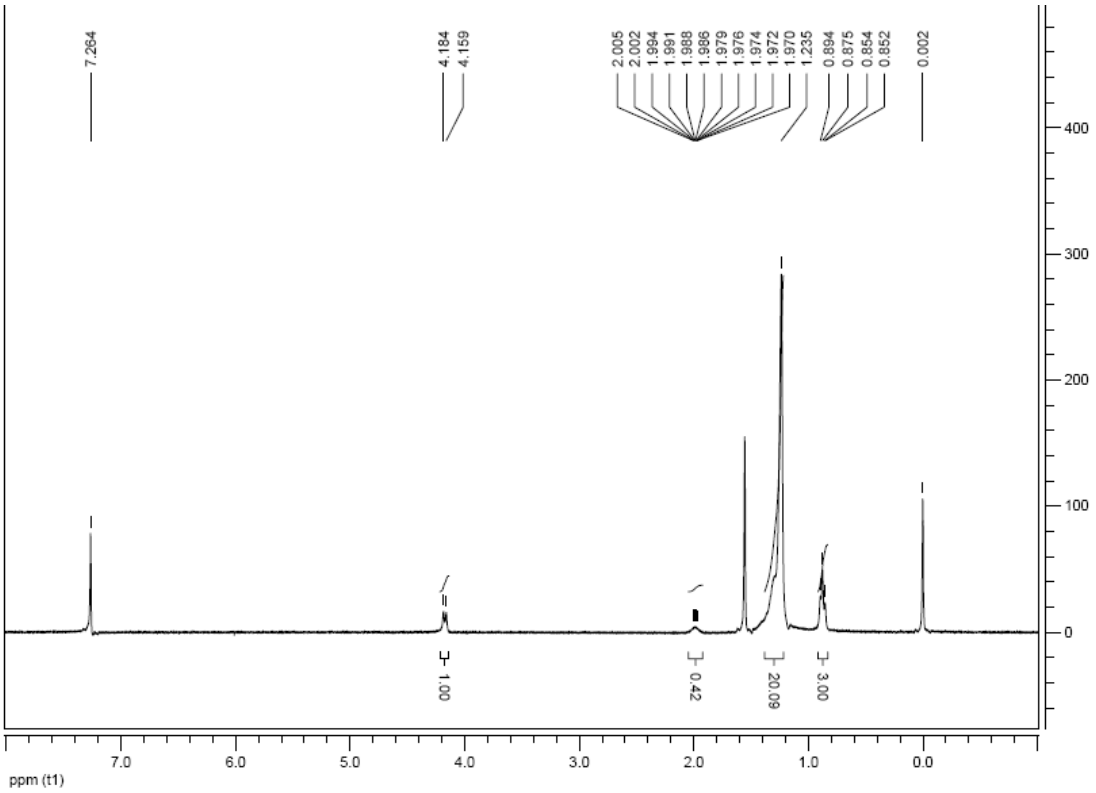
Although some mild and/or time-saving syntheses of TBNDA have been recently reported,[5-7] our synthetic method for TBNDA can afford product with higher yield (96%) and higher purity.[1]

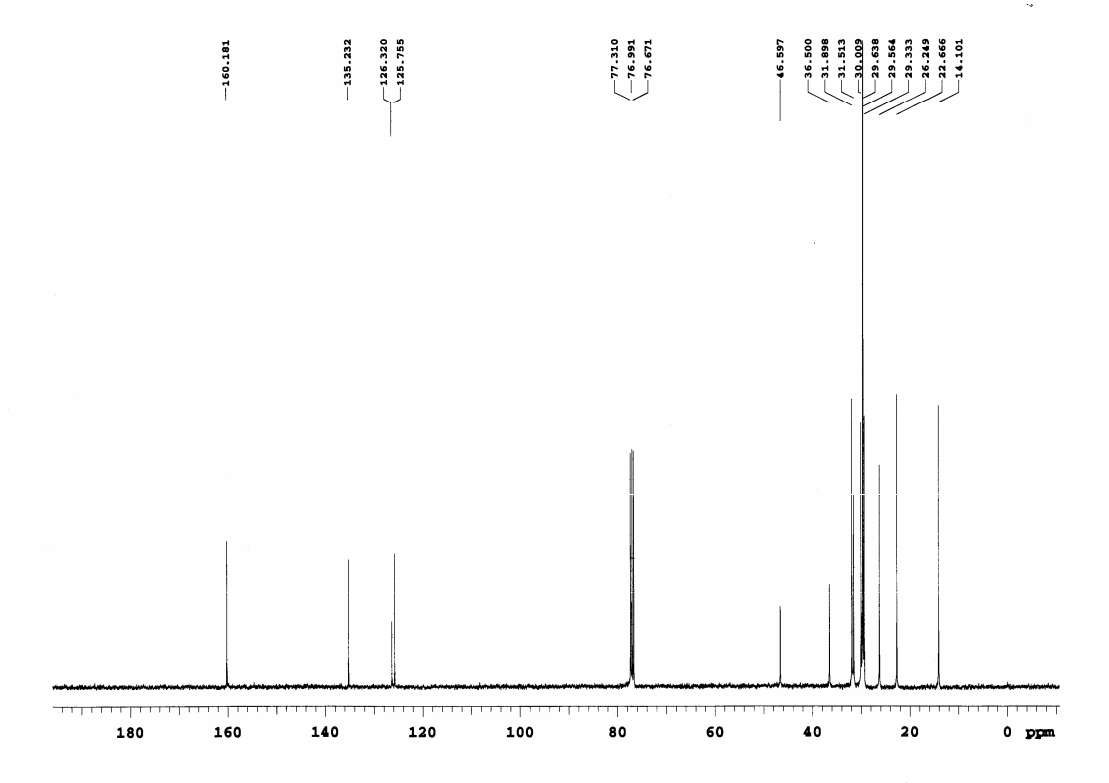
4,5,9,10-tetrabromo-2,7-bis(2-decyltetradecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (3)

As shown in Scheme S1, compound **3** was prepared from 2-decylt-etradecylamine[2] and TBNDA[1] according to the published procedure for the synthesis of 4,5,9,10-Tetrabromo-2,7-dioctyl-benzo[lmn][3,8]phenanthroline-1,3,6,8-tetraone.[1] **3** was obtained as a yellow solid in 19% yield (calculated from TBNDA): MS (MALDI-TOF) *m*/*z* 1257.6 (M^+); ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 0.852–0.894 (m, 6H, $-CH_3$), 1.287–1.409 (m, 8H, CH_2), 1.235 (b, 40H, CH_2), 1.970-2.005 (m, 1H, CH), 4.159–4.184 (d, J = 7.50 Hz, 2H, $-CH_2-N$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.10, 22.67, 26.25, 29.33, 29.56, 29.64, 30.01, 31.50, 31.90, 36.50, 46.60, 125.75, 126.32, 135.23, 160.18 (CO).

The MS, ^{1}H-NMR and ^{13}C-NMR spectra of 3 are listed as follows:



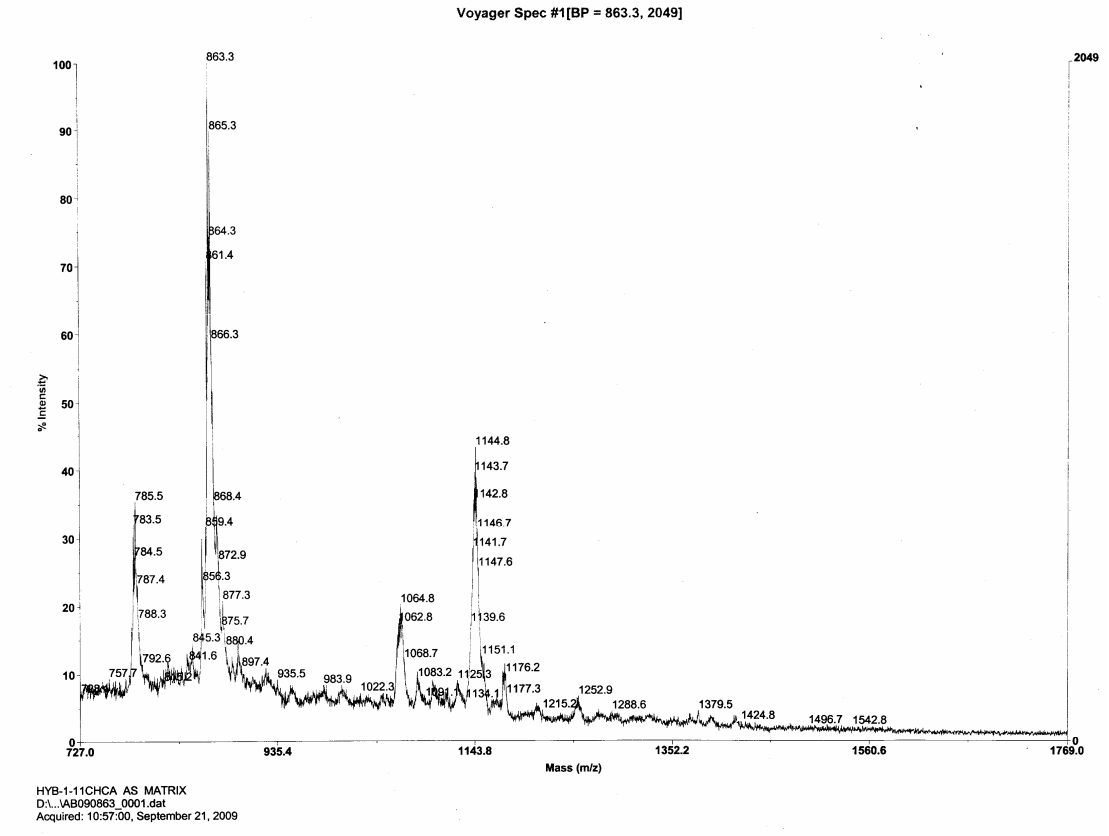

7.264
4.184
4.159
2.005
2.002
1.994
1.991
1.988
1.986
1.979
1.976
1.974
1.972
1.970
1.235
0.894
0.875
0.854
0.852
0.002
1.00
0.42
20.09
3.00
ppm (t1)

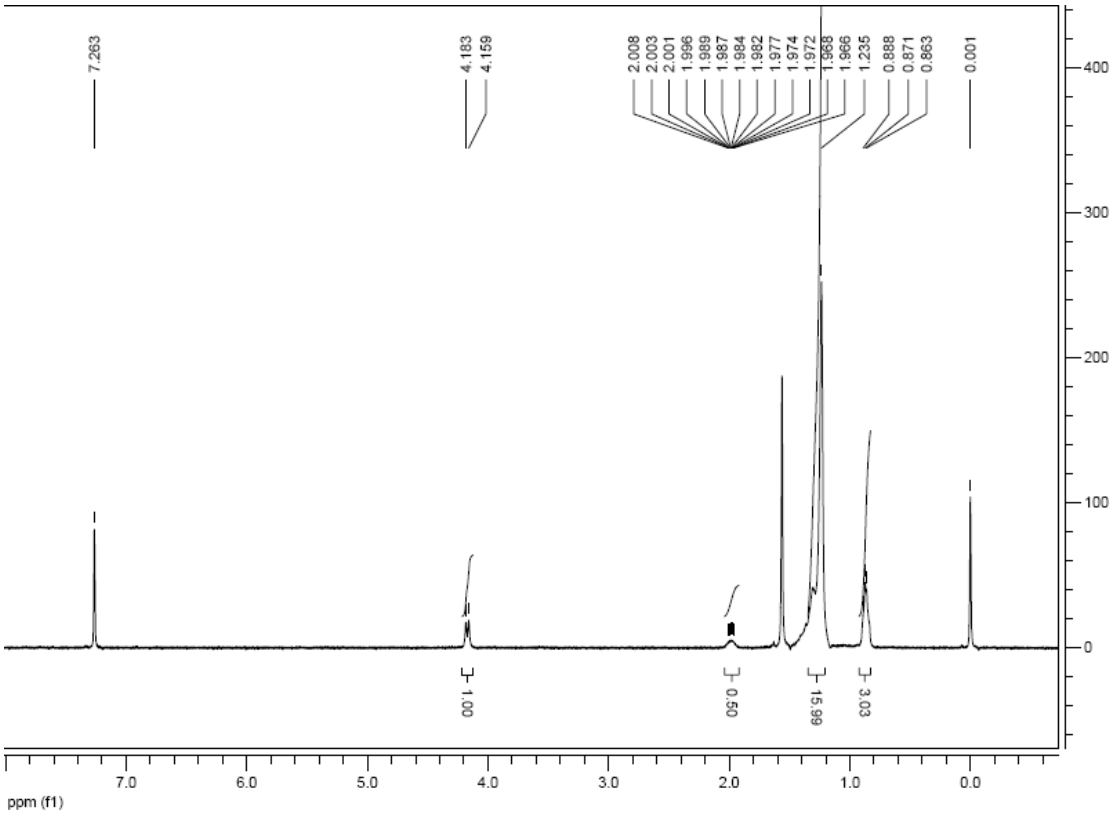

160.181
135.232
126.320
125.755
77.310
76.991
76.671
46.597
36.500
31.898
31.513
30.009
29.638
29.564
29.333
26.249
22.666
14.101
ppm

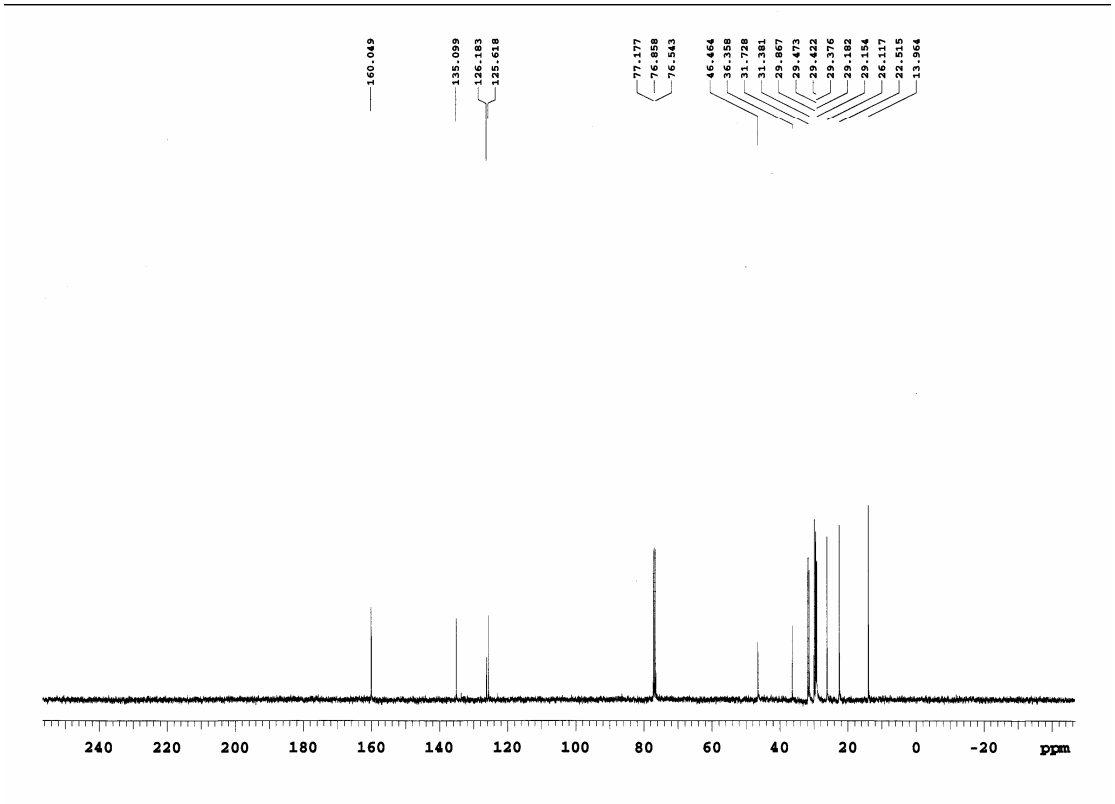
4,5,9,10-tetrabromo-2,7-bis(2-octyldodecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (4)

As shown in Scheme S1, compound **4** was prepared from 2-octyl-dodecylamine[3] and TBNDA[1] according to the published procedure for the synthesis of 4,5,9,10-Tetrabromo-2,7-dioctyl-benzo[lmn][3,8]phenanthroline-1,3,6,8-tetraone.[1] **4** was obtained as a yellow solid in 33% yield (calculated from TBNDA): MS (MALDI-TOF) *m*/*z* 1144.8 (M^+); ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 0.863–0.888 (m, 6H, $-CH_3$), 1.235 (b, 32H, CH_2), 1.966-2.008 (m, 1H, CH), 4.159–4.183 (d, J = 7.20 Hz, 2H, $-CH_2-N$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.96, 22.52, 26.12, 29.15, 29.18, 29.38, 29.42, 29.87, 31.38, 31.73, 36.36, 46.46, 125.62, 126.18, 135.10, 160.05 (CO).

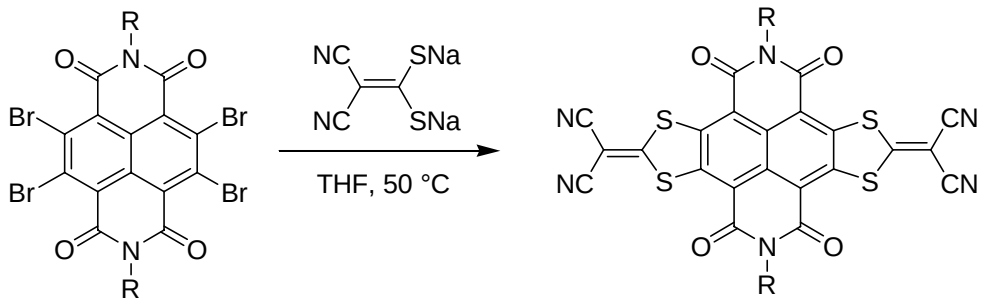
The MS, ^{1}H-NMR and ^{13}C-NMR spectra of 4 are listed as follows:




7.263
4.183
4.159
2.008
2.003
2.001
1.996
1.989
1.987
1.984
1.982
1.977
1.974
1.972
1.968
1.966
1.235
0.888
0.871
0.863
0.001
1.00
0.59
6.99
3.03
ppm (f1)


160.049
135.099
126.183
125.618
77.177
76.858
76.543
46.464
36.358
31.728
31.381
29.867
29.473
29.422
29.376
29.182
29.154
26.117
22.515
13.964
ppm

Synthesis of compounds 1 and 2.



3
4

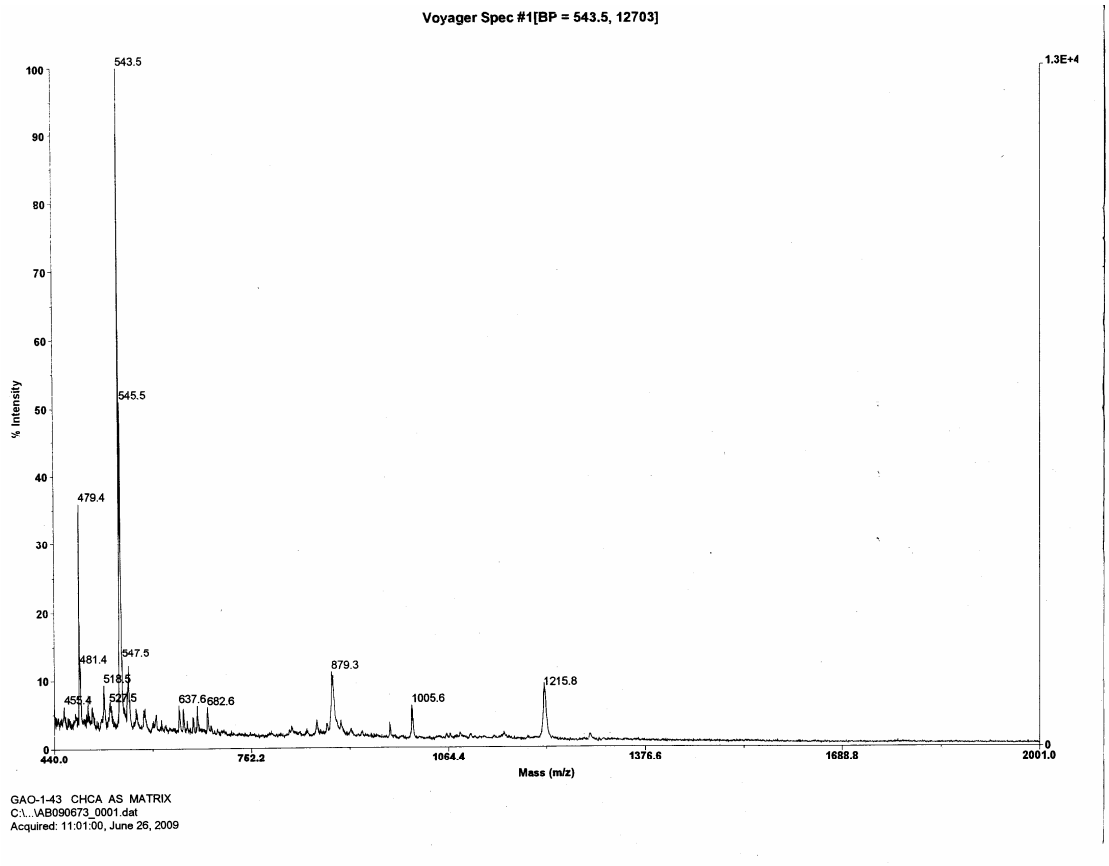
1 R = 2-Decyl-tetracosyl
2 R= 2-Octyl-dodecyl

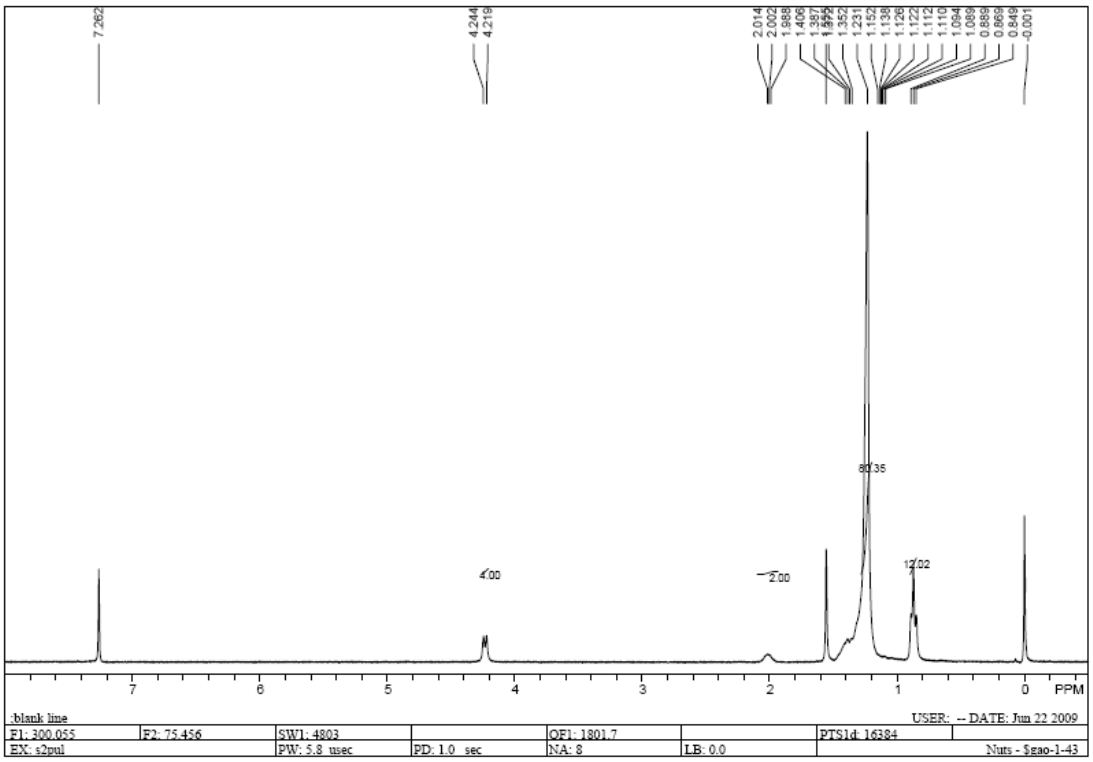
Scheme S2

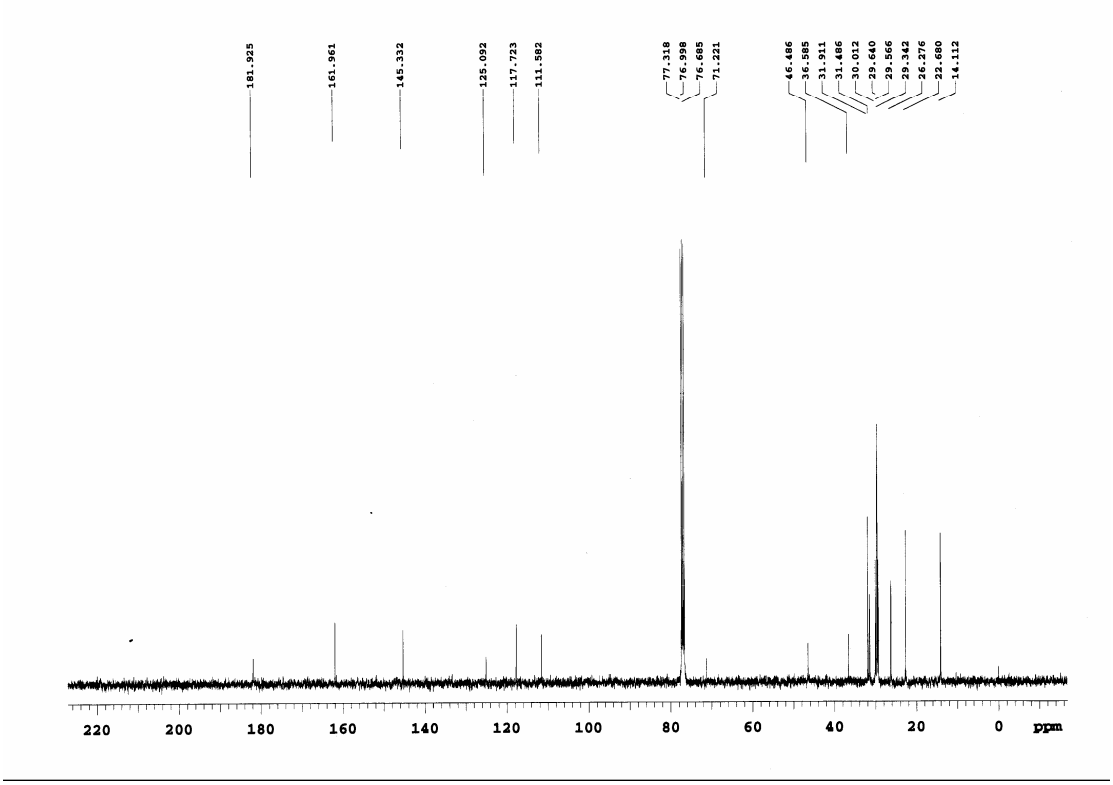
N,N′-bis(2-decyltetradecyl)-2,2′-Naphtho[2,3-d:6,7-d′]bis[1,3]dithiol-2,7-diyliden e-bismalononitrile-1,4,5,8-tetracarbonyl diimide (1)

Under a nitrogen atmosphere, a solution of **3** (126 mg, 0.1 mmol) and sodium 1,1-dicyanoethylene-2,2-dithiolate[4] (56 mg, 0.3 mmol) in THF (20 mL) was stirred at 50 °C for 1 hour. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. Chromatography of the residue on a silica gel column with CH_2Cl_2/petroleum ether (3/1) as eluent afforded 60 mg (50 %) of **1** as a brownish red solid: Mp: 240 °C (from DSC); MS (MALDI-TOF) *m*/*z* 1215.8 (M^+); ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 0.849–0.889 (m, 6H, $-CH_3$), 1.231 (b, 40H, CH_2), 1.988-2.014 (m, 1H, CH), 4.219–4.244 (d, J = 7.50 Hz, 2H, $-CH_2-$N); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.11, 22.68, 26.28, 29.34, 29.57, 29.64, 30.01, 31.49, 31.91, 36.59, 46.49, 71.22 (=$C(CN)_2$), 111.58, 111.72 (C≡N), 125.09, 145.33, 161.96 (C=O), 181.93 (=CS_2).; FT-IR (KBr, cm^{-1}) ν 2924 (s), 2852, 2213 (C≡N), 1686, 1641 (vs), 1537, 1493, 1485, 1457 (s), 1397, 1338, 1299, 1220 (s), 791, 728, 683, 635, 491, 463.; Anal. Calcd. for $C_{70}H_{98}N_6O_4S_4$: C, 69.15; H, 8.12; N, 6.91. Found: C, 69.41; H, 8.37; N, 6.67.

The MS, ^{1}H-NMR, ^{13}C-NMR and IR spectra of 1 are listed as follows:






181.925
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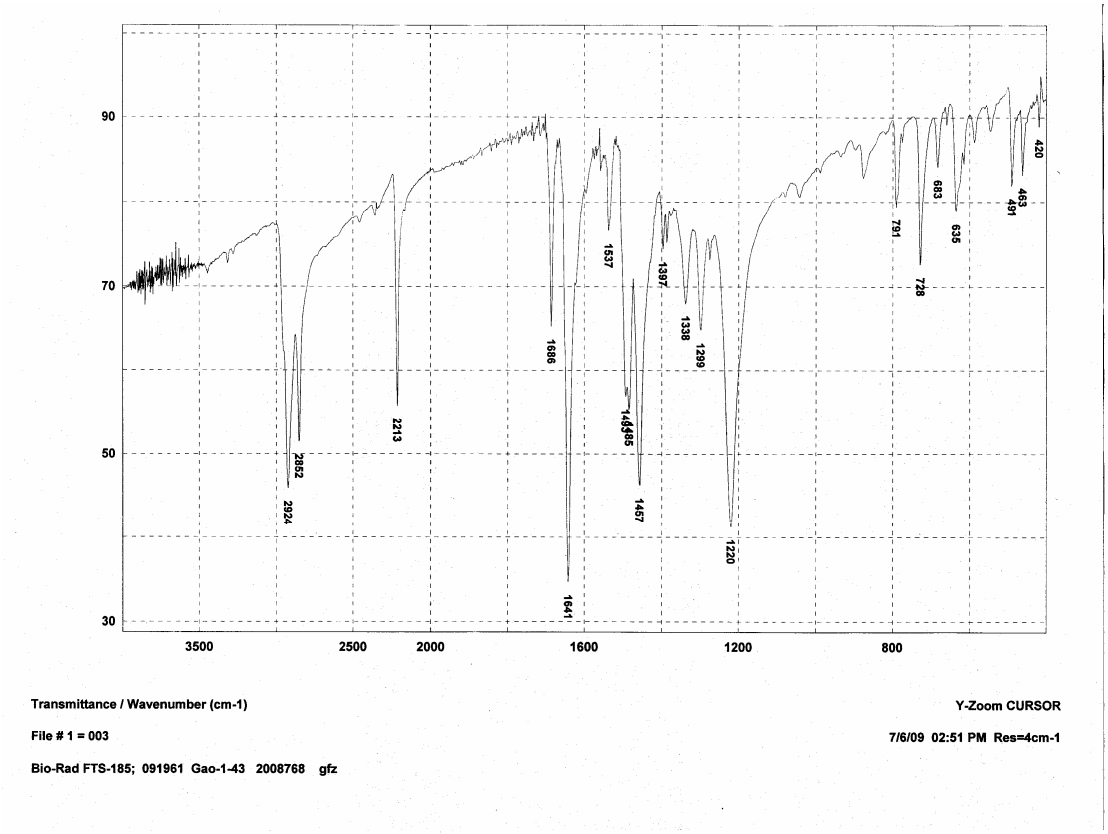
145.332
125.092
117.723
111.582
77.318
76.998
76.685
71.221
46.486
36.585
31.911
31.486
30.012
29.640
29.566
29.342
26.276
22.680
14.112
220
200
180
160
140
120
100
80
60
40
20
0
ppm


90
70
50
30
3500
2500
2000
1600
1200
800
2924
2852
2213
1686
1641
1537
1485
1457
1397
1338
1299
1220
791
728
683
635
491
463
420
Transmittance / Wavenumber (cm-1)
File # 1 = 003
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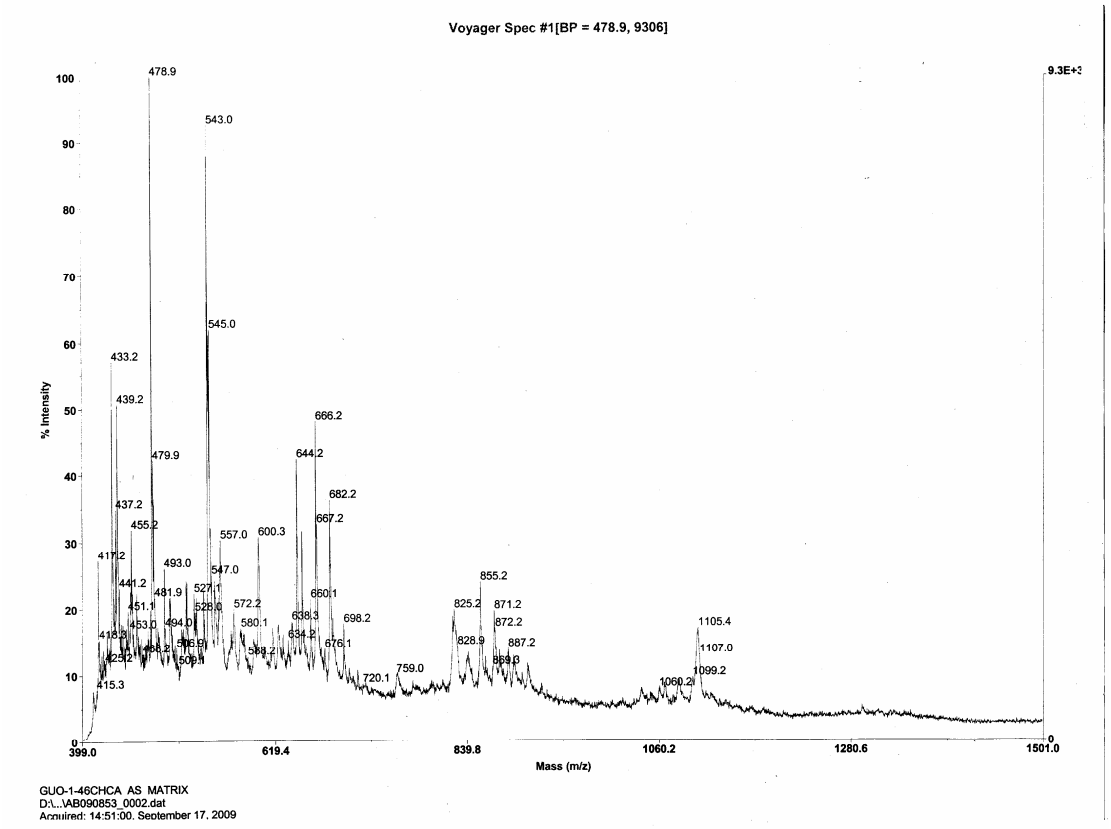
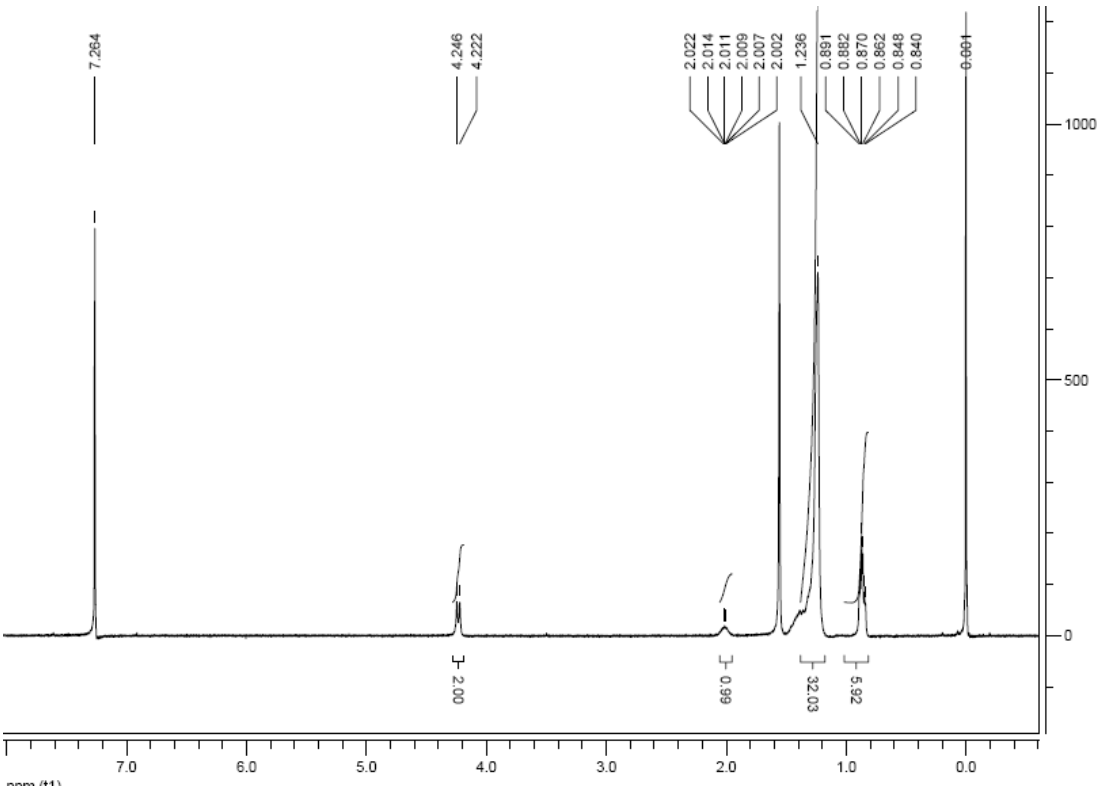
Y-Zoom CURSOR
7/6/09 02:51 PM Res=4cm-1

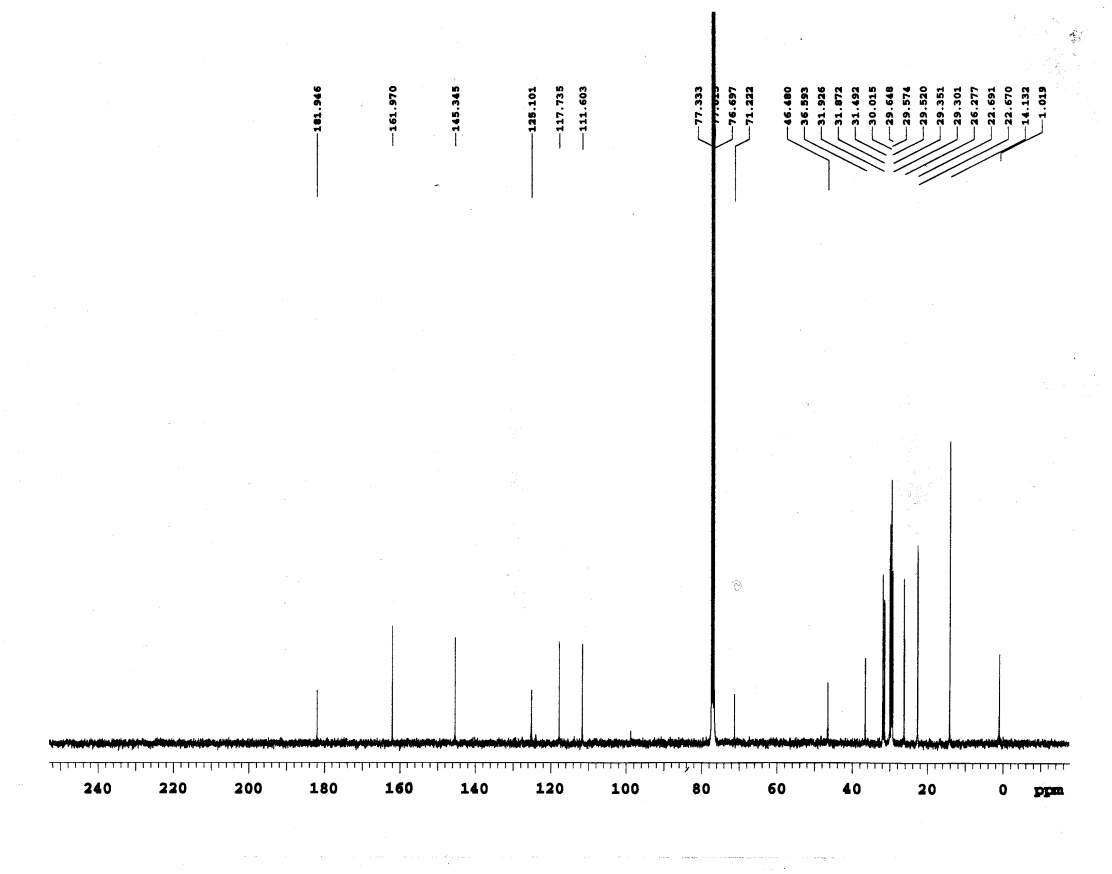
N,N′-bis(2-octyldodecyl)-2,2′-Naphtho[2,3-d:6,7-d′]bis[1,3]dithiol-2,7-diylidene-bismalononitrile-1,4,5,8-tetracarbonyl diimide (2)

A mixture of **4** (343 mg, 0.3 mmol), sodium 1,1-dicyanoethylene-2,2-dithiolate[4] (168 mg, 0.9 mmol) and THF (50 mL) was stirred at 50 °C for 1 hour under a nitrogen atmosphere, then cooled to room temperature. After removing the solvent under reduced pressure, the residues were separated via column chromatography (silica gel, CH_2Cl_2/petroleum ether (2/1)). **2** (175 mg) was obtained as a purple solid with the yield of 53%: Mp: 265 °C (from DSC); MS (MALDI-TOF) *m*/*z* 1105.4 (M^+); ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 0.840–0.891 (m, 6H, $-CH_3$), 1.236 (b, 32H, CH_2), 2.002-2.022 (m, 1H, CH), 4.222–4.246 (d, J = 7.20 Hz, 2H, $-CH_2-$N); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.13, 22.67, 22.69, 26.28, 29.30, 29.35, 29.52, 29.57, 29.65, 30.02, 31.49, 31.87, 31.93, 36.59, 46.48, 71.22 (=$C(CN)_2$), 111.60, 111.74 (C≡N), 125.10, 145.35, 161.97 (C=O), 181.95 (=CS_2).; FT-IR (KBr, cm^{-1}) ν 2924 (s), 2852, 2212 (C≡N), 1687, 1641 (vs), 1536, 1492, 1484, 1458 (s), 1397, 1338, 1299, 1221 (vs), 790, 728, 683, 635, 490, 463.; Anal. Calcd. for $C_{62}H_{82}N_6O_4S_4$: C, 67.48; H, 7.49; N, 7.62. Found: C, 67.38; H, 7.58; N, 7.56.

The MS, ^{1}H-NMR, ^{13}C-NMR and IR spectra of 2 are listed as follows:



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111.603
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76.697
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26.277
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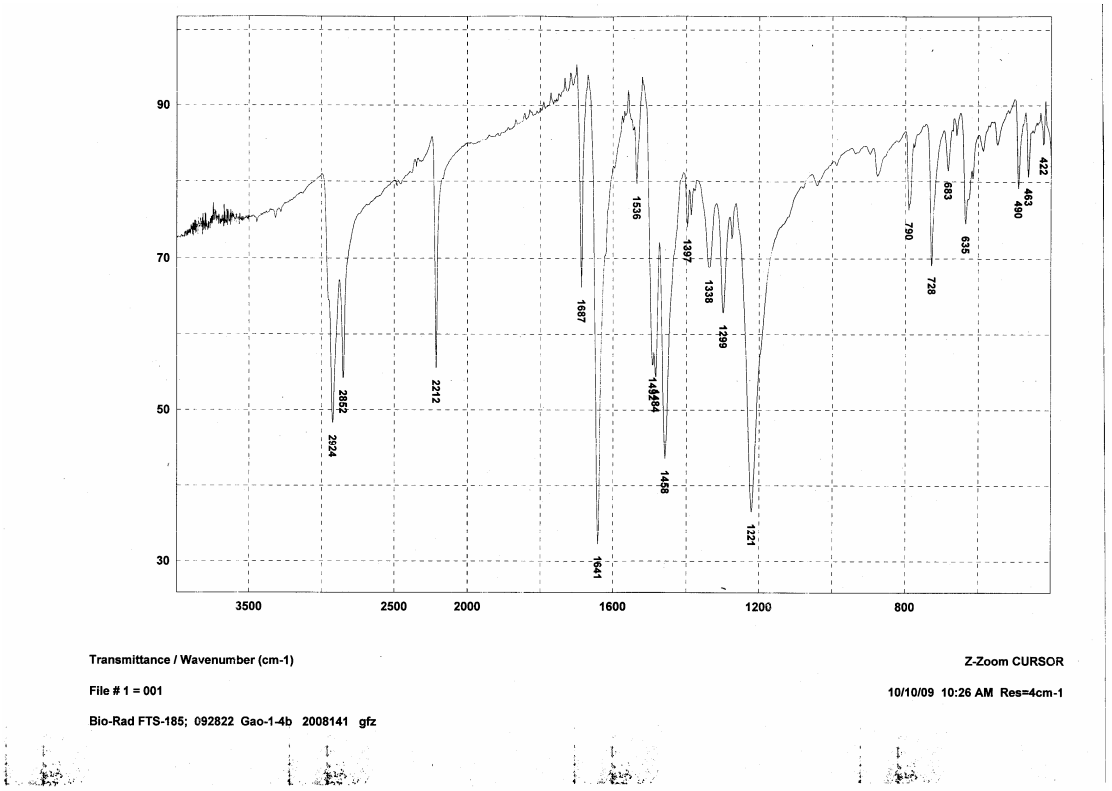
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1687
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1338
1299
1221
790
728
683
635
490
463
422
Transmittance / Wavenumber (cm-1)
File # 1 = 001
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Z-Zoom CURSOR
10/10/09 10:26 AM Res=4cm-1

References

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7. Bell, T. D. M.; Yap, S.; Jani, C. H.; Bhosale, S. V.; Hofkens, J.; De Schryver, F. C.; Langford, S. J.; Ghiggino, K. P. *Chem. Asian J.* **2009**, *4*, 1542-1550.

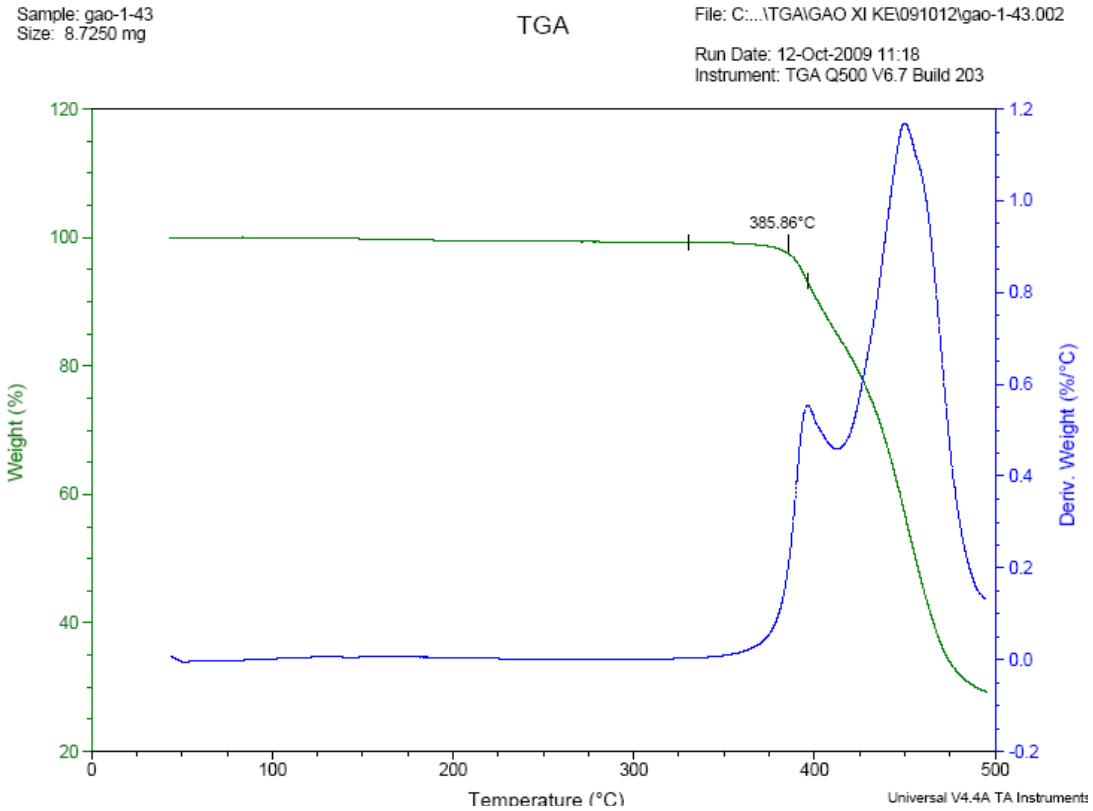

Figure S1. TGA plots of **1**.

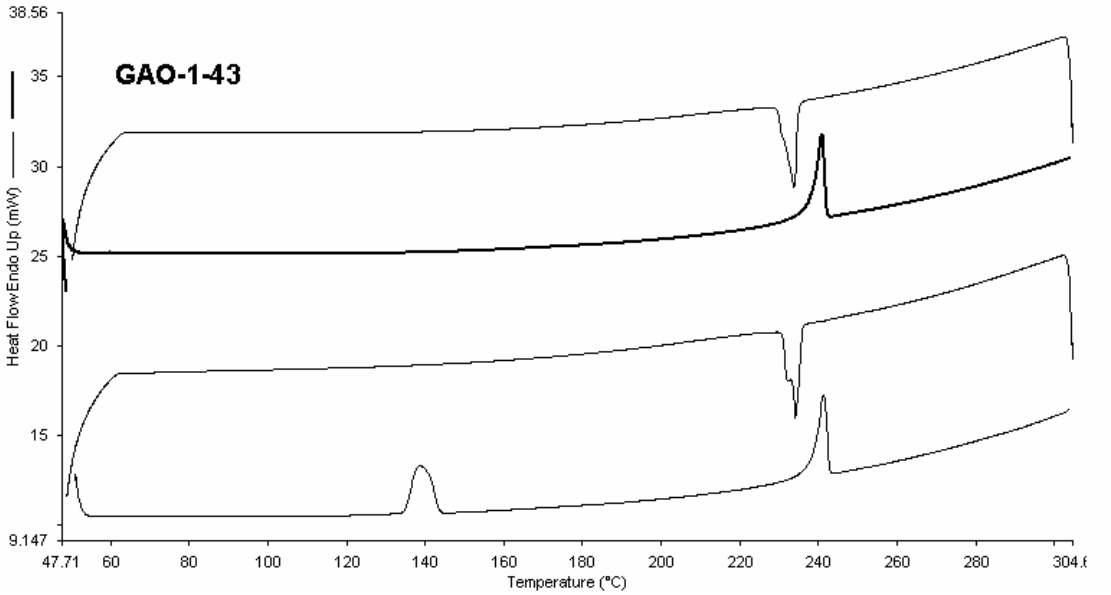

Figure S2. DSC spectra of **1**, in which the bottom spectrum is the first heating-cooling cycle and the top one is the second heating-cooling cycle.

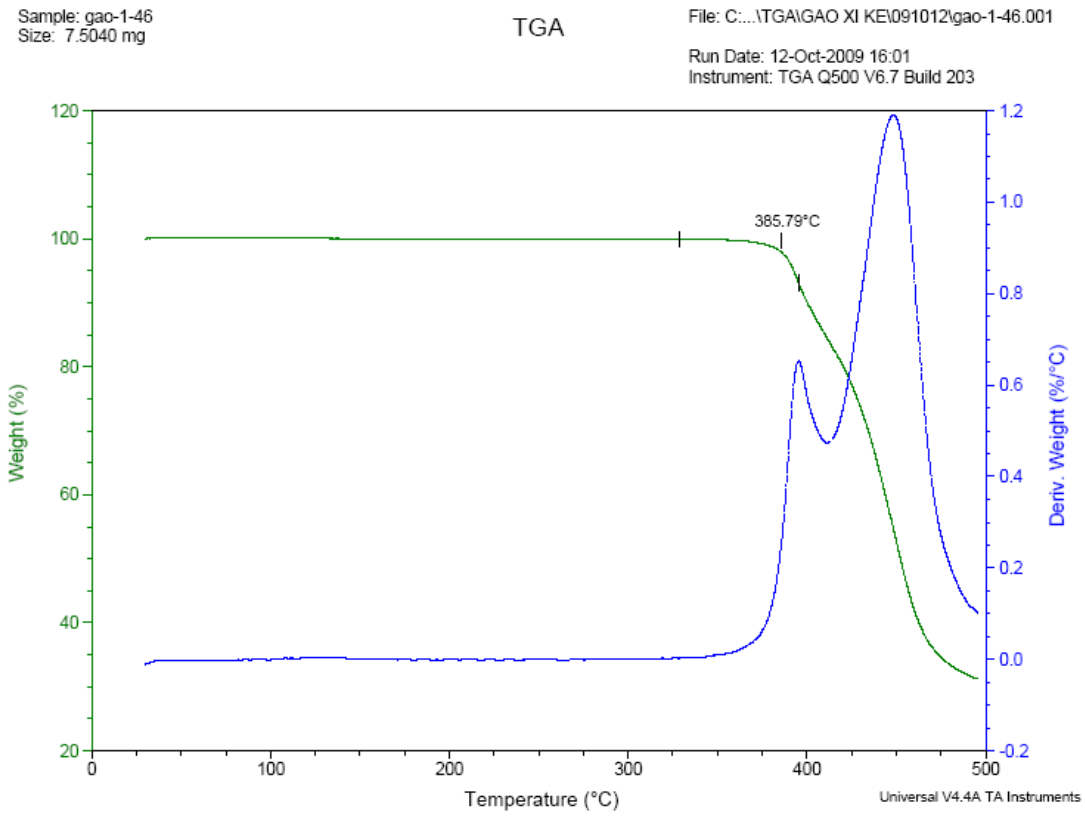

Figure S3. TGA spectrum of **2**.

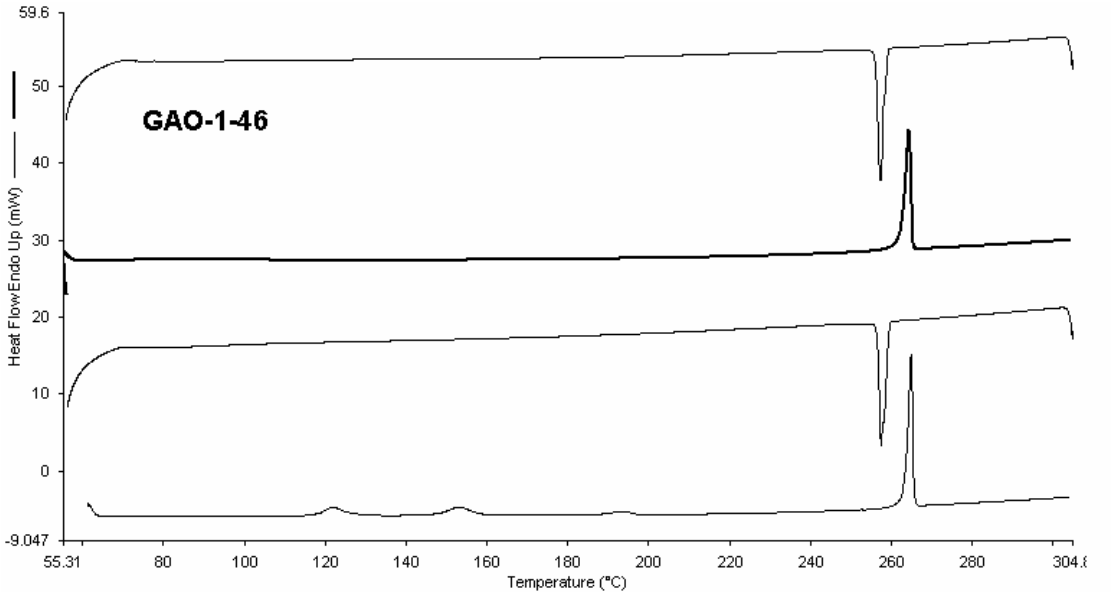

Figure S4. DSC spectra of **2**, in which the bottom spectrum is the first heating-cooling cycle and the top one is the second heating-cooling cycle.

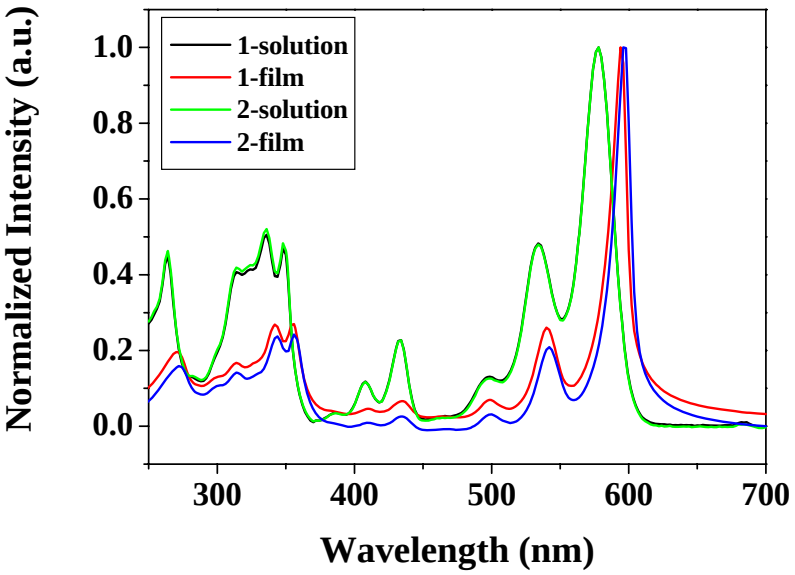

Figure. S5 Electronic absorption spectra of **1** (black, in CH_2Cl_2; red, as-spun film) and **2** (green, in CH_2Cl_2; blue, as-spun film).

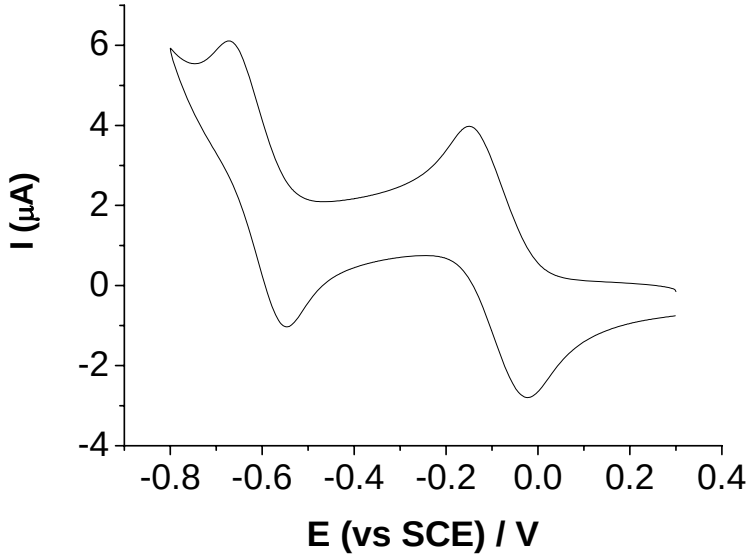

Figure. S6 Cyclic voltammogram of **1** (0.001 mol/L in CH_2Cl_2, 0.1mol/L Bu_4NPF_6, scan rate 50 mV/s)

OTFT Device Fabrication and Measurements

An n-type heavily doped Si wafer with a SiO_2 layer of 300 nm and a capacitance of 11 nF cm^{-2} was used as the gate leectrode and dielectric layer. The thin films (40–60 nm) of **1** and **2** were deposited on octadecyltrichlorosilane (OTS)-treated SiO_2/Si substrates by spin-coating of their $CHCl_3$ solutions (10 mg/mL). Next, the thin films were annealed at 120 °C, 160 °C, or 180 °C. Gold (or silver) source and drain contacts (30 nm in thickness) were deposited by vacuum evaporation on the organic layer through a shadow mask, affording a bottom-gate top-contact device configuration. The channel length (L) and width (W) were 50 μm and 3 mm, respectively. Electrical measurements of OTFT devices were carried out at room temperature in air using a Keithley 4200 semiconductor parameter analyzer. The mobilities were determined in the saturation regime by using the equation $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, and V_T is the threshold voltage.

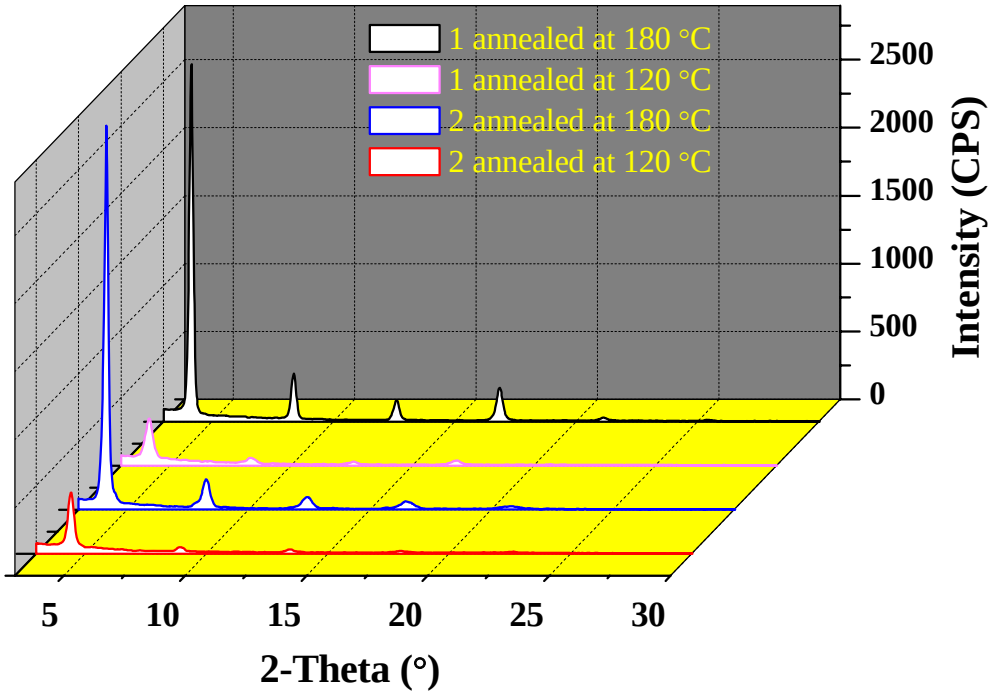

Figure S7. XRD patterns of spin-coated thin films of **1** and **2** annealed at 120 and 180°C.

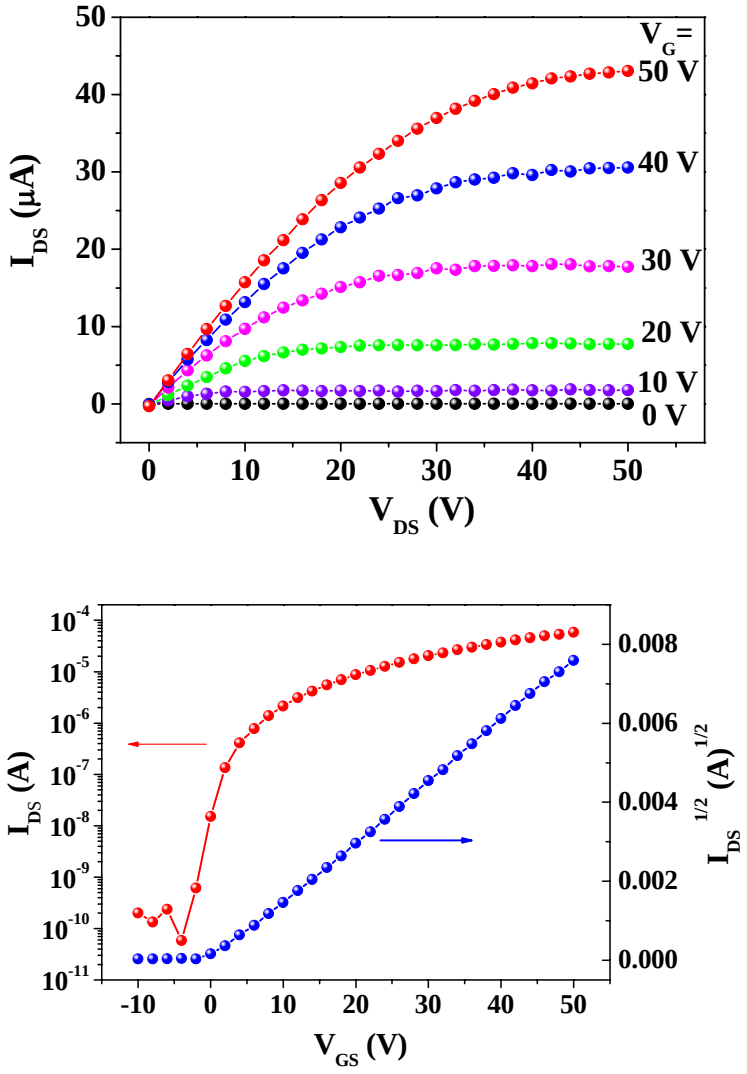

Figure S8. The output (top) and transfer (bottom) characteristics of an Au-contact OTFT device based on **1** (annealed at 160 °C), with μ_e = 0.16 $cm^2V^{-1}s^{-1}$, I_{on}/I_{off} = 10^6 and V_T = 2 V (V_{DS} = 60 V).

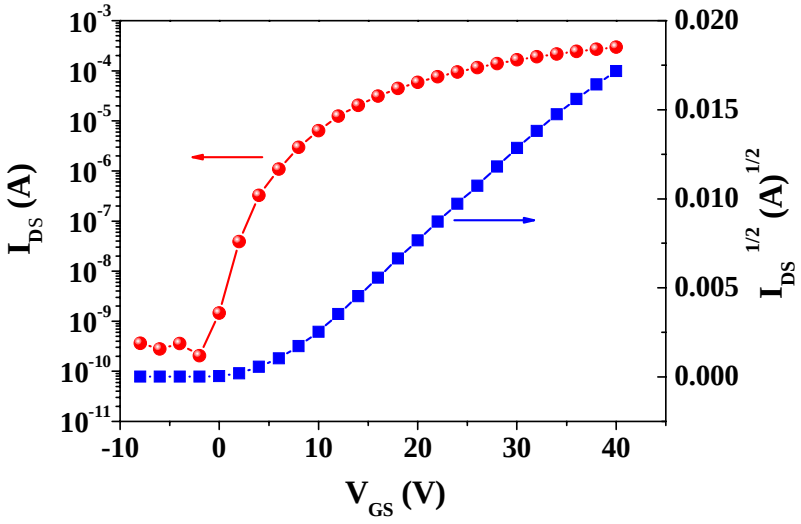

Figure S9. The transfer plots of an Ag-contact OTFT devices based on **2** (annealed at 180 °C), which affords the highest electron mobility of 0.51 $cm^2V^{-1}s^{-1}$ with I_{on}/I_{off} = 10^6 and V_T = 5.2 V (V_{DS} = 60 V, scanning region of V_{GS} is –10 V~40 V).

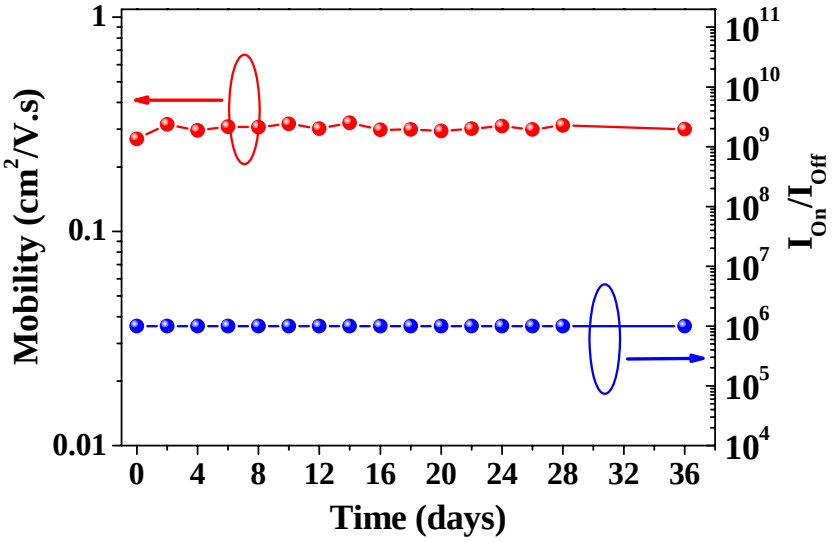

Figure S10. Air-stability measurements of an Au-contact OTFT device based on **2** (annealed at 180 °C) over a period of 36 days. Top: charge carrier mobilities as a function of time. Bottom: on/off ratios as a function of time.

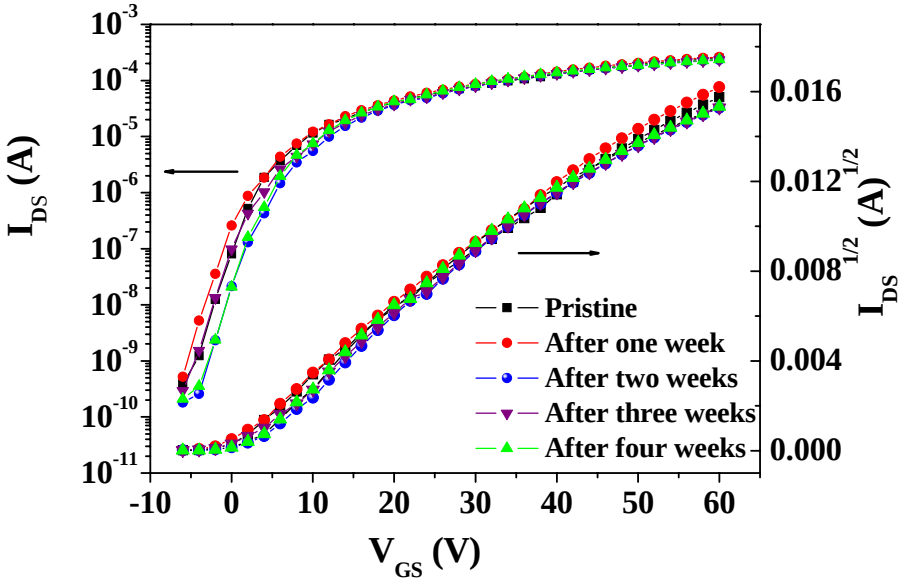

Figure S11. The transfer plots of the same OTFT device based on **2** (Figure S10), tested weekly during a period of four weeks under ambient conditions.

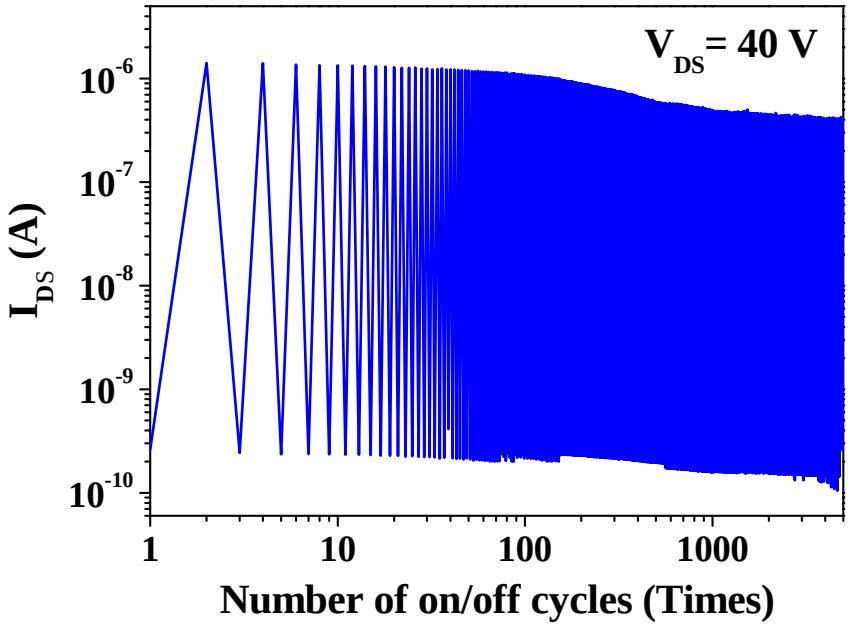

Figure S12: Electrical characteristics of a **2**-based OTFT during cycle-test in air (5000 times, between V_{GS} = 0 V (off) and V_{GS} = 40 V (on)).