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SUPPORTING INFORMATION

Molecular aggregation of naphthalimide organic semiconductors assisted by amphiphilic and lipophilic interactions: a joint theoretical and experimental study

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Contents

1. Materials, instruments and methods

All the chemicals were purchased from commercial suppliers and used without further purification. Compounds1-(2-bromothiophen-3-yl)-2,5,8,11-tetraoxadodecane[1], 2-(2-ethylhexyl)-1H-indeno[6,7,1-def]isoquinoline-1,3,6,7(2H)-tetraone[2]and 3′,4′- Dinitro-3,3′′-dioctyl-[2,2′;5′,2′′]terthiophene[3]were obtained as previously described.

Toluene was freshly distilled over sodium/benzophenone under nitrogen and Chloroform over calcium hydride before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300, and AMX 500 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the residual non-deuterated solvent frequencies (CDCl$_3$: δ 7.26 ppm for ^{1}H, δ 77.0 ppm for ^{13}C). UV–vis absorption spectra of the compounds in HPLC dichloromethane solutions at 20 ^{o}C were recorded on a Varian Cary 50 UV–vis spectrophotometer. Mass spectra were recorded on a MAT95 XP (FAB/IE) or Bruker Reflex 2 (MALDI-TOF). Cyclic voltammograms were recorded in an inert atmosphere in electrochemical workstation at a scan rate of 100 mV·s^{-1} at 20 ^{o}C using tetrabutylammoniumhexafluorophosphate(TBAHFP, 0.1 mol L^{-1}) as supporting electrolyte in dichloromethane. Polymer-precoated platinum electrode, platinum–wire electrode, and Ag/Ag$^+$ electrode were used as working electrode, an auxiliary electrode, and reference electrode, respectively. Potentials were recorded versus Fc/Fc$^+$.

Absorption spectra were recorded with a Cary 5000 spectrophotometer from Varian operating in a maximal 175–3300 nm range.2Me-THFsolutions were prepared to obtain the spectra at different temperatures from room conditions to 79 K in a cryostat OPTISTAT from Oxford instruments.

Emission and excitation spectra were measured using a spectrofluorometer from Edinburgh Analytical Instrument (FLS920P) equipped with a pulsed xenon flash-lamp, Xe900, of 400 mW. 2Me-THF solutions were prepared to obtain the spectra at different temperatures from room conditions to 79 K in a cryostat OPTISTAT from Oxford instruments.

Scanning electron microscopy images were obtained on a JEOL JSM 6335F microscope working at 10kVand on anHelios Nanolab 650 Dual Beam from FEI company. The latter is a microscope with a Schottky field emission source for SEM (FESEM) and a Tomohawk focused ion beam (FIB). The microscope is equipped with energy dispersive X-ray detector (EDS) and electron backscatter diffraction detector (EBSD) from Oxford.

TGA and DSC measurements were performed at a heating rate of 10 ºC/min under nitrogen flow on a TA Instruments SDT Q600 and a METTLER TOLEDO DSC822 respectively.

X-ray diffraction was performed in a Panalytical X'Pert PRO diffractometer with Cu tube and primary beam monochromator (lambda Kα=1.5406 Å) operated at 45 kV, 40 mA, programmable divergence slit working in fixed mode, and fast linear detector (X'Celerator) working in scanning mode. Samples were deposited on "zero background" silicon sample holders and measured in reflection geometry.

The electrical measurements were made by using Linkam cells which require small amounts of materials and allow the formation of very uniform films. They consist of two indium tin oxide (ITO)-coated parallel glass plates with a gap of 5.0 μm and an effective area of 0.81 cm^2 which were capillary-filled with **NIP-3T$_{\mathbf{Amphi}}$** and **NIP-3T$_{\mathbf{Lipo}}$**. The mobility of charge carriers at RT was determined by employing the time of flight (TOF) technique. The excitation source was a pulsed Nd:YAG laser (7 ns, 10 Hz) operating at 355 nm, which is close to the wavelength of maximum absorbance of the **NIP-3T** derivatives.

Photoconductivity measurements were also carried out in the spectral region of maximum absorption. A high-pressure mercury vapor lamp and a 12 nm bandwidth interferential filter with maximum transmission at 365 nm was the light source selected to illuminate the samples. The applied field was 0.4 V/μm and the light intensity 1 mW/cm^2. Current densities in the absence of light, j_{dark}, and under illumination, j_{light}, were measured. Then, corrected photocurrent densities, j_{phot}, defined as $j_{\mathrm{light}} - j_{\mathrm{dark}}$, and photosensitivities, $S = j_{\mathrm{phot}} / j_{\mathrm{dark}}$, were calculated.

The theoretical study was carried out in the frame of density functional theory (DFT) using the B3LYP functional[1,2] and the 6-31G** basis set[3,4] as implemented in the Gaussian 09 program.[5] The geometry optimizations were performed without any symmetry constraints. On the basis of the resulting ground-state geometries, harmonic vibrational frequencies were calculated analytically at the same theoretical level. The reorganization energies, were calculated directly from the relevant points on the potential energy surfaces using the standard procedure detailed in the literature.[6]

To gain further insight into the aggregation behavior of the NPI dimers, DFT calculations were conducted for two different dimers for each molecule (i.e.,**NIP-3T$_{\mathbf{Amphi}}$** and **NIP-3T$_{\mathbf{Lipo}}$**), one in a parallel (P) and the other in an antiparallel (AP) fashion. The more recently developed long-range corrected Coulomb attenuated method of B3LYP (CAM-B3LYP functional)[7] was used to evaluate the dimer ground-state geometries. Vertical electronic excitation energies were computed by using the time-dependent DFT (TD-DFT) approach[8] on the previously optimized dimer geometries. CAM-B3LYP and wB97XD[9] functionals were employed to examine the excited-state properties.

The transfer integrals of the optimized dimers were calculated at the B3LYP/6-31G(d,p) level, according to the approach described by Valeev et al.[10] with the corresponding matrix elements evaluated with Gaussian 09.Note that the coupling values depend on the functional used and generally increase with the increasing percentage of Hartree-Fock exchange in the functional.[11] We also computed the transfer integrals for model cofacial dimers of unsubstituted naphthalimide-fused thienopyrazine when one of the molecules is translated along its short axis.

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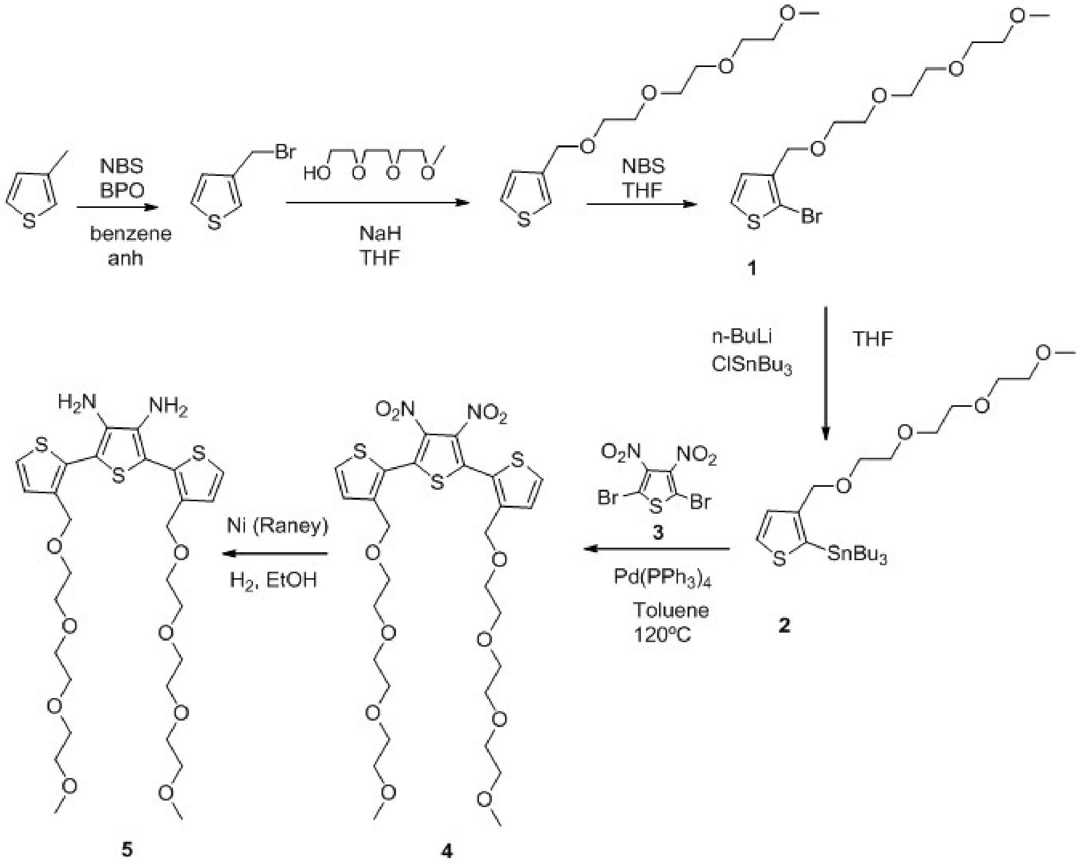
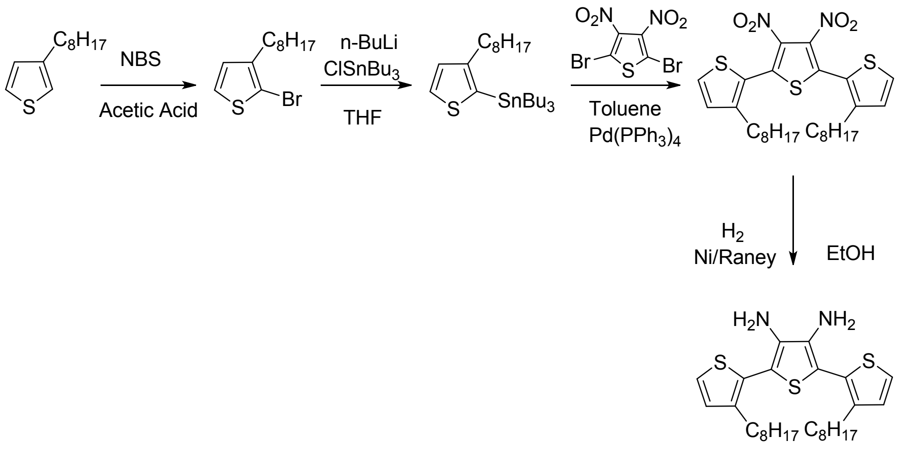
2. Synthetic details

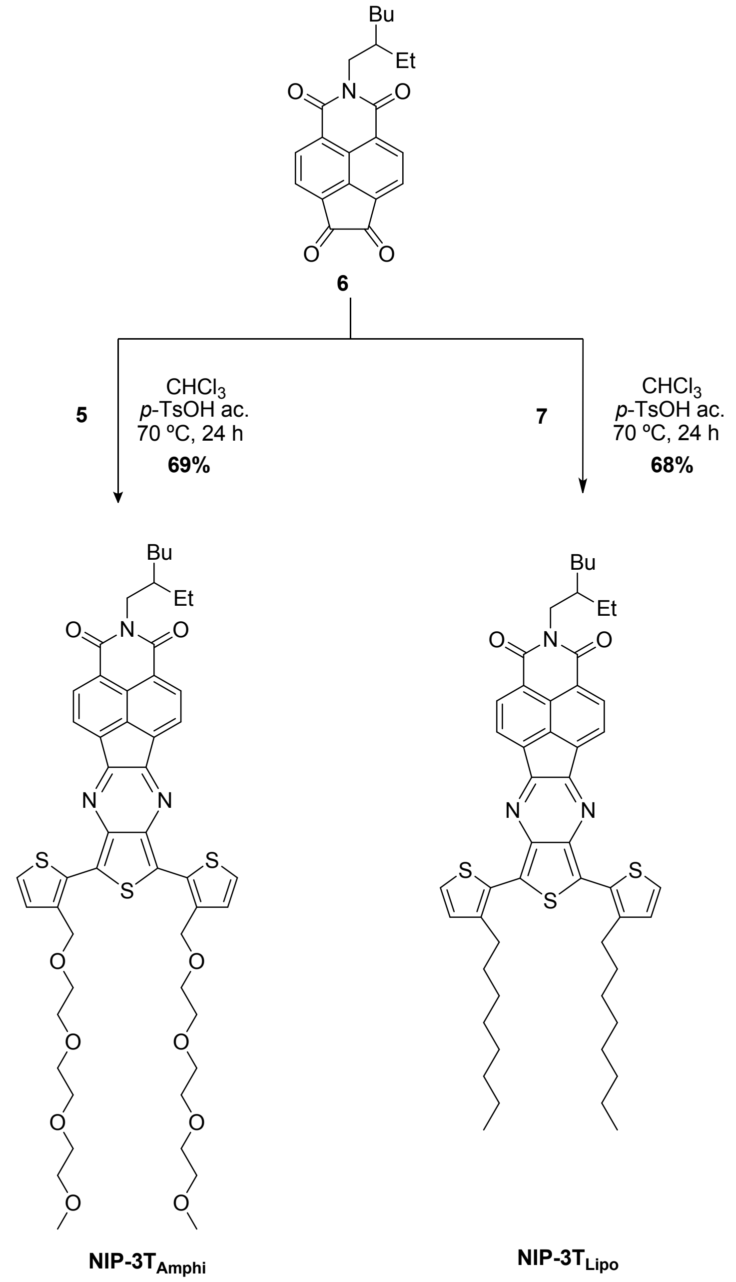
All compounds were synthesized according to Schemes S1-S3.



Scheme 1

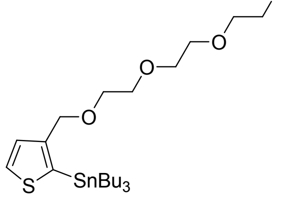


Scheme 2



Scheme 3

<u>(3-(2,5,8,11-tetraoxadodecyl)thiophen-2-yl)tributylstannane (2)</u>



1-(2-bromothiophen-3-yl)-2,5,8,11-tetraoxadodecane[1](500 mg, 1.47 mmol)**1** was dissolved in 26 mL of THF under argon atmosphere in the absence of light. The mixture was cooled at -78ºC and *n*-BuLi (1.25 mL, 1.47 mmol) was added dropwise. The reaction was stirred for 1.5 h at that temperature. Then tributyltin chloride (0.4 mL, 1.47 mmol) was added and the mixture was stirred at room temperature overnight. After the removal of the solvent under reduced pressure the crude was dissolved in dichloromethane and washed with NH_4Cl and water. The organic layer was dried over $MgSO_4$, filtered and finally solvent was removed in vacuo. The crude reaction was chromatographied on basic alumina (hexane) and the tributyltin chloride excess was distilled off yielding 538 mg (67%) of product as a clear oil.

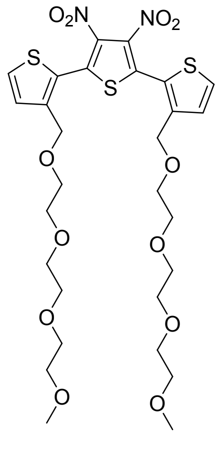
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm)= 7.55 (d, *J*= 4.7 Hz, 1H,*Ar*), 7.23 (d, *J*= 4.7 Hz, 1H,*Ar*), 4.53 (s, 2H), 3.70-3.57 (m, 10H), 3.55 (m, 2H), 3.37 (s, 3H), 1.53 (m, 6H), 1.39-1.23 (m,6 H), 1.20-1.05 (m, 6H), 0.88 (t, *J*= 7.3 Hz, 9H).

^{13}C-NMR (75MHz, $CDCl_3$) δ (ppm)=146.7, 134.9, 131.1, 129.3, 72.1, 70.8, 70.4, 69.4, 59.2, 29.1, 27.4, 13.8, 11.2.

FTIR (ATR, CH_2Cl_2), υ (cm^{-1}) = 2955, 2922, 2865, 1675, 1522, 1459, 1417, 1372, 1292, 1248, 1198, 1105, 1029, 960, 873, 698, 669, 596.

MS (EI) m/z = calc. 550.21; found 573.28 ($M+Na^+$).

1,1'-(3',4'-dinitro-[2,2':5',2''-terthiophene]-3,3''-diyl)bis(2,5,8,11-tetraoxadodecane) (4)



A mixture of (3-(2,5,8,11-tetraoxadodecyl)thiophen-2-yl)tributylstannane**2** (400 mg, 0.73 mmol), 2,5-dibromo-3,4-dinitrothiophene (80.8 mg, 0.24 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (5%) were dissolved in 27 mL of degassed anhydrous toluene. The mixture was refluxed under stirring for 21 h under argon. Then, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude was dissolved in dichloromethane and washed with NH_4Cl and water. The organic layer was dried over $MgSO_4$, filtered and finally the solvent was removed in vacuum. The solid was purified by column chromatography on silica gel (ethyl acetate/methanol) yielding 150.5 mg (90%) of**4** as a brown oil.

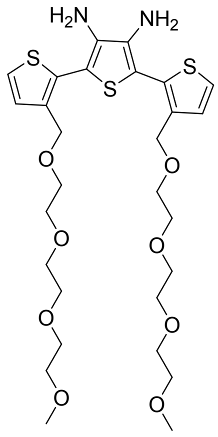
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm)= 7.53 (d, *J*= 5.2 Hz, 2H, *Ar*), 7.21 (d, *J*= 5.2 Hz, 2H, *Ar*), 4.54 (s, 4H), 3.64-3.61 (m, 20H), 3.54 (m, 4H), 3.36 (s, 6H).

^{13}C-NMR (75MHz, $CDCl_3$) δ (ppm)= 142.3, 138.6, 134.2, 129.6, 129.5, 123.0, 72.0, 70.7, 70.6, 70.5, 70.0, 67.2, 59.1.

FTIR (ATR, CH_2Cl_2), υ (cm^{-1}) = 3098, 2921, 2854, 1717, 1539, 1461, 1400, 1378, 1349, 1323, 1246, 1198, 1104, 1030, 965, 847, 800, 751, 704.

MS (MALDI TOF)(*m/z*) =calc.690.15; found713.04 ($M+Na^+$).

3,3''-di(2,5,8,11-tetraoxadodecyl)-[2,2':5',2''-terthiophene]-3',4'-diamine (5)



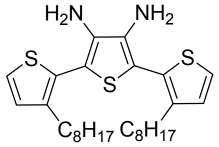
A solution of 1,1'-(3',4'-dinitro-[2,2':5',2''-terthiophene]-3,3''-diyl)bis(2,5,8,11-tetraoxadodecane)**4** (95 mg, 0.14mmol)and Ni/Raney in ethanol was stirred under hydrogen pressure (1 atm) at 12ºC overnight. The mixture was filtered over celite under argon atmosphere, washed with chloroform and acetone. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to a quantitatively yieldof **5** as a brown solid. Due to instability diamine **5** was used without further purification.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm)= 7.28 (d, *J* =6 Hz, 2H), 7.13 (d, *J* =6 Hz, 2H), 4.48 (s, 4H), 3.67 (m, 20H), 3.54 (m, 4H) 3.35 (s, 6H).

FTIR (ATR, CH_2Cl_2), υ (cm^{-1}) = 3414, 3348, 2922, 2855, 1737, 1636, 1507, 1451, 1392, 1349, 1529, 1198, 1175, 1100, 1024, 937, 846, 801, 735, 697, 658, 638, 544.

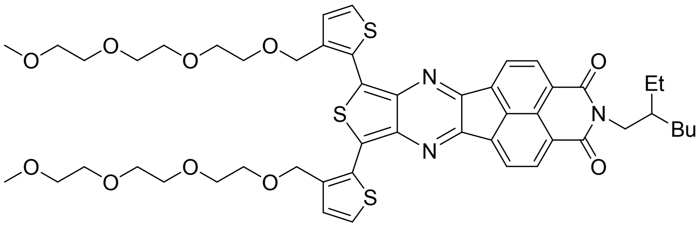
MS (EI) m/z = calc. 630.2; found630.2 ($M^{+\cdot}$)

3′,4′- Diamino-3,3′′-dioctyl-[2,2′;5′,2′′]terthiophene (7)



A solution of 3′, 4′- Dinitro-3,3′′-dioctyl-[2,2′; 5′,2′′] terthiophene[3](116.3 mg, 0.21 mmol) and Ni/Raney in 14 mL of ethanol was stirred under hydrogen pressure (1 atm) at 12ºC overnight. The mixture was filtered over celite under argon, washed with dichloromethane and the organic layer was dried over $MgSO_4$. Solvent was removed under reduced pressure to a quantitatively yield of **6** as a brown solid. Due to instability diamine **6** was used without further purification. Compound **7** was checked by comparison with reported data[3].

NIP-3T$_{Amphi}$



To a 20 mL chloroform solution of 2-(2-ethylhexyl)-1H-indeno[6,7,1-def]isoquinoline-1,3,6,7(2H)-tetraone[2] (50.8 mg, 0.14 mmol), a catalytic amount of ac. *p*-TsOH.(10%) was added and the mixture was heated at 70ºC. When the temperature reached 50ºC a solution in chloroform of 3,3''-di(2,5,8,11-tetraoxadodecyl)-[2,2':5',2''-terthiophene]-3',4'-diamine**4** (99.5 mg, 0.157 mmol) was added. The mixture turns quickly to a red wine color. The mixture was stirred for 22 h at 70ºC. Then the crude was washed with Na_2CO_3, the organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The solid was chromatographied on silica gel (dichloromethane/methanol) to obtain 93.0 mg (69%) of a blue solid.

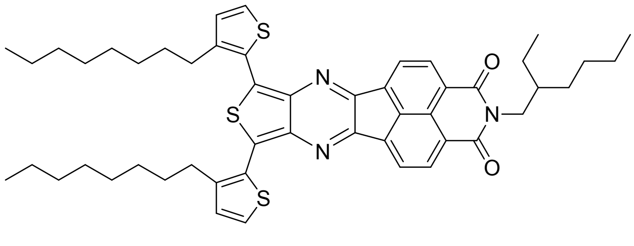
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.68 (d, *J*=6.0 Hz, 2H), 8.40 (d, *J*=6.0, 2H), 7.52 (d, *J*=6.0 Hz, 2H), 7.33 (d, *J*=6.0 Hz, 2H), 4.85 (s, 4H), 4.18-4.13 (m, 2H), 3.66-3.59 (m, 18H), 3.53-3.49 (m, 6H), 3.34 (s,6H), 1.95 (m, 1H), 1.43-1.25 (m, 8H), 0.97-0.87 (m,6H)

^{13}C-NMR (75MHz, $CDCl_3$) δ (ppm)=163.9, 153.6, 138.3, 138.2, 136.9, 136.7, 132.7, 129.9, 129.6, 128.2, 127.8, 125.6, 124.2, 122.0, 72.0, 70.8, 70.7, 70.6, 69.8, 68.1, 59.1, 44.5, 38.3, 30.9, 29.8, 28.8, 24.2, 23.2, 14.2, 10.8.

FTIR (ATR, CH_2CL_2), υ (cm^{-1}) = 2925, 2855, 1705, 1669, 1538, 1460, 1408, 1374, 1332, 1230, 1108, 991, 874, 829, 715, 686, 634, 578.

MS (MALDI TOF HR) (*m/z*) = calc. 957.3; found 980.3 (M^+Na^+)

NIP-3T$_{Lipo}$



To a 27 mL chloroform solution of 2-(2-ethylhexyl)-1H-indeno[6,7,1-def]isoquinoline-1,3,6,7(2H)-tetraone[2] (62.6 mg, 0.17mmol), a catalytic amount of ac.*p*-

TsOH (10%) was added and the mixture was heated at 70ºC. When the temperature reached 50ºC a solution in chloroform of 3´,4´- Diamino-3,3´´-dioctyl-[2,2´;5´,2´´]terthiophene**6** (104.3 mg, 0.21 mmol) was added. The mixture turns quickly to a dark purple color. The mixture was stirred for 22 h. Then, the solvent was removed under reduced pressure and the crude was dissolved in dichloromethane and washed with Na_2CO_3. The organic layer was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The solid was chromatographied on silica gel (dichloromethane/hexane) to obtain 97.6 mg (68%) of a blue solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm)= 8.65 (d, *J*=7.4 Hz, 2H), 8.37 (d, *J*=7.4 Hz, 2H), 7.49 (d, *J*=5.2 Hz, 2H), 7.10 (d, *J*=5.2 Hz, 2H), 4.15 (m, 2H), 2.96-2.93 (m, 4H), 1.94 (s, 1H), 1.83-1.73 (m, 4H), 1.40-1.21 (m, 28 H), 0.97-0.80 (m, 12H).

^{13}C-NMR (75MHz, $CDCl_3$) δ (ppm)= 164.0, 153.2, 142.4, 138.0, 136.9, 136.8, 132.6, 129.8, 128.2, 127.6, 127.2, 123.9, 121.9, 38.3, 32.0, 30.7, 29.9, 29.7, 29.4, 24.2, 23.2, 22.8, 14.3, 14.2, 10.8.

FTIR (ATR, CH_2Cl_2), υ (cm^{-1}) =2956, 2925, 2855, 1736, 1702, 1666, 1637, 1458, 1327, 1235, 1169, 1082, 857, 821, 748, 698.

MS (MALDI TOF HR) (*m/z*) = calc.829.3769; found. 830.3824($M+H^+$).

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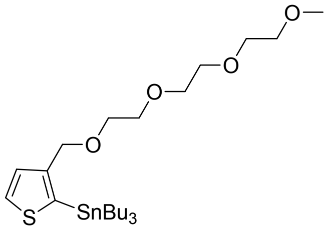
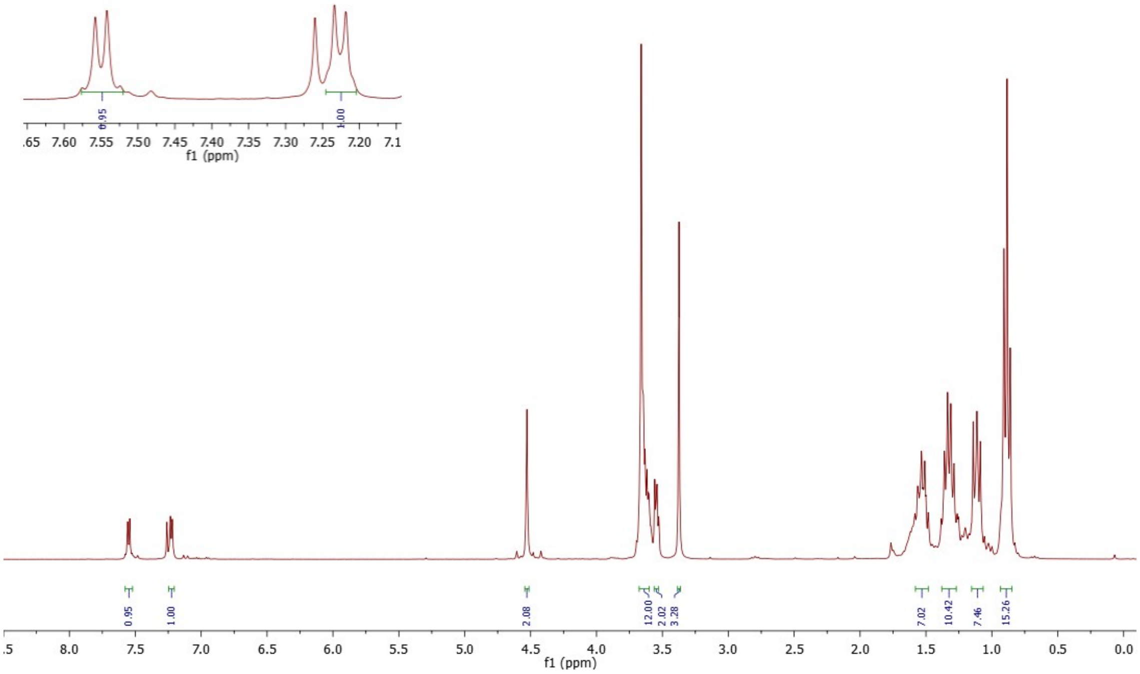
3. Characterization

3.1. NMR, FT-IR and MS characterization

(3-(2,5,8,11-tetraoxadodecyl)thiophen-2-yl)tributylstannane (2)



^{1}H-NMR



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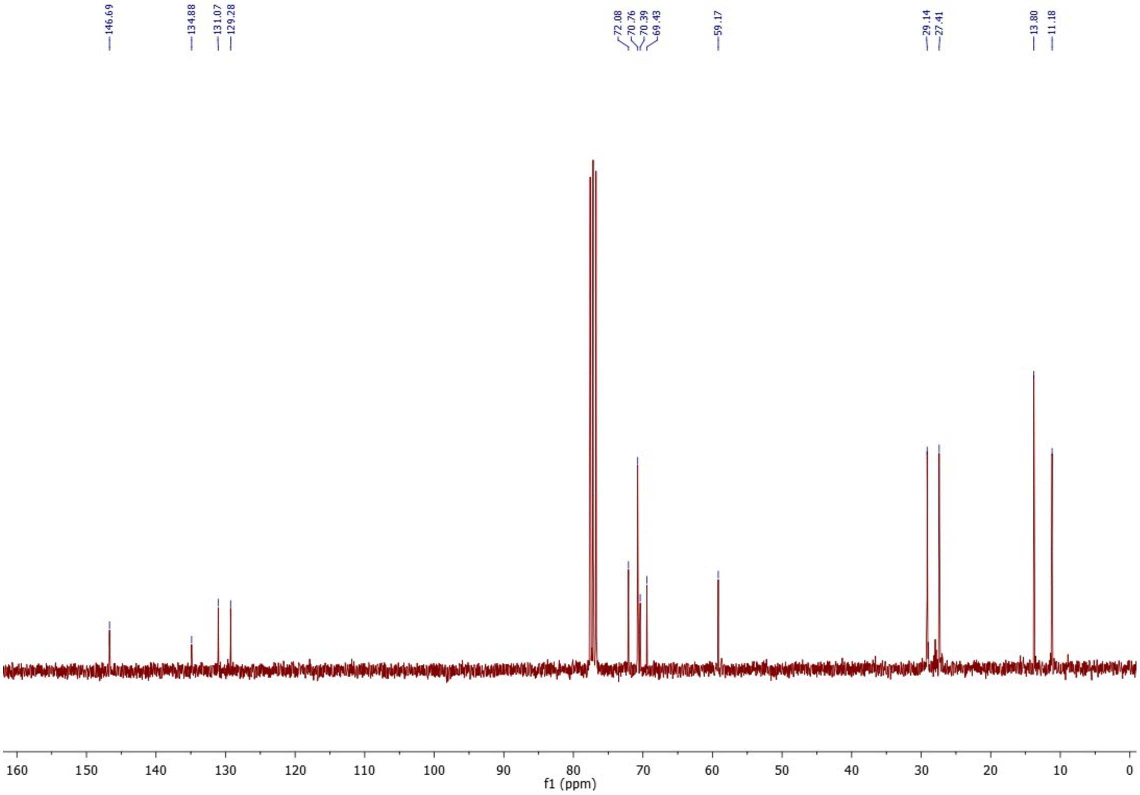
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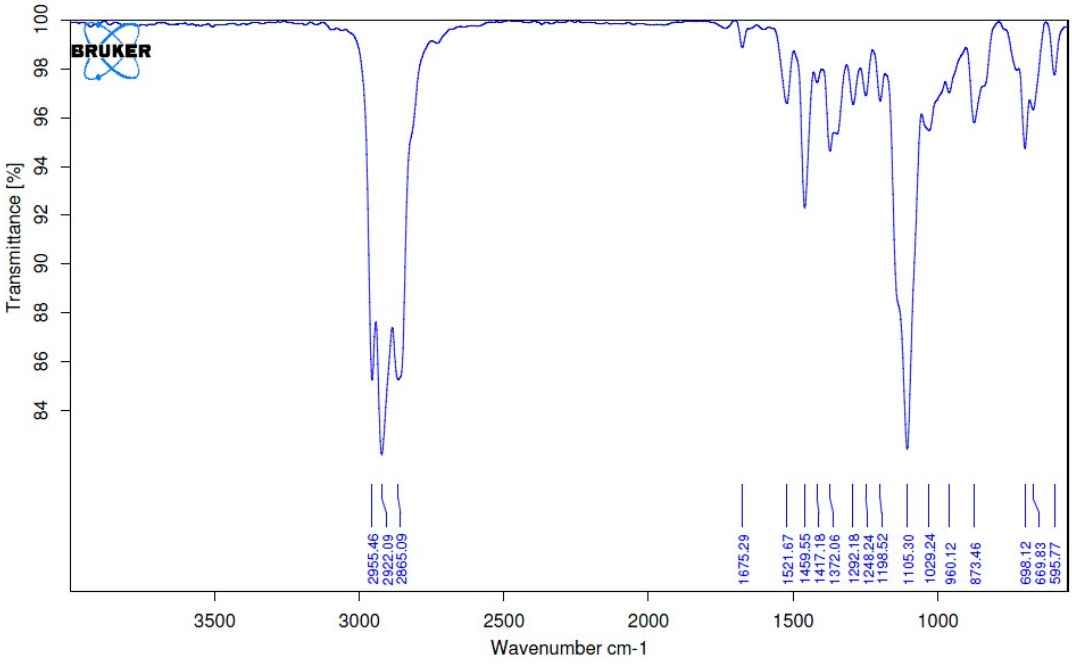
129.28
72.08
70.76
70.39
69.43
59.17
29.14
27.41
13.80
11.18
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

IR


BRUKER
Transmittance [%]
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98
96
94
92
90
88
86
84
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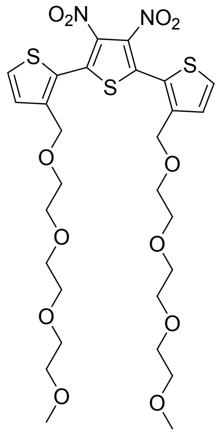
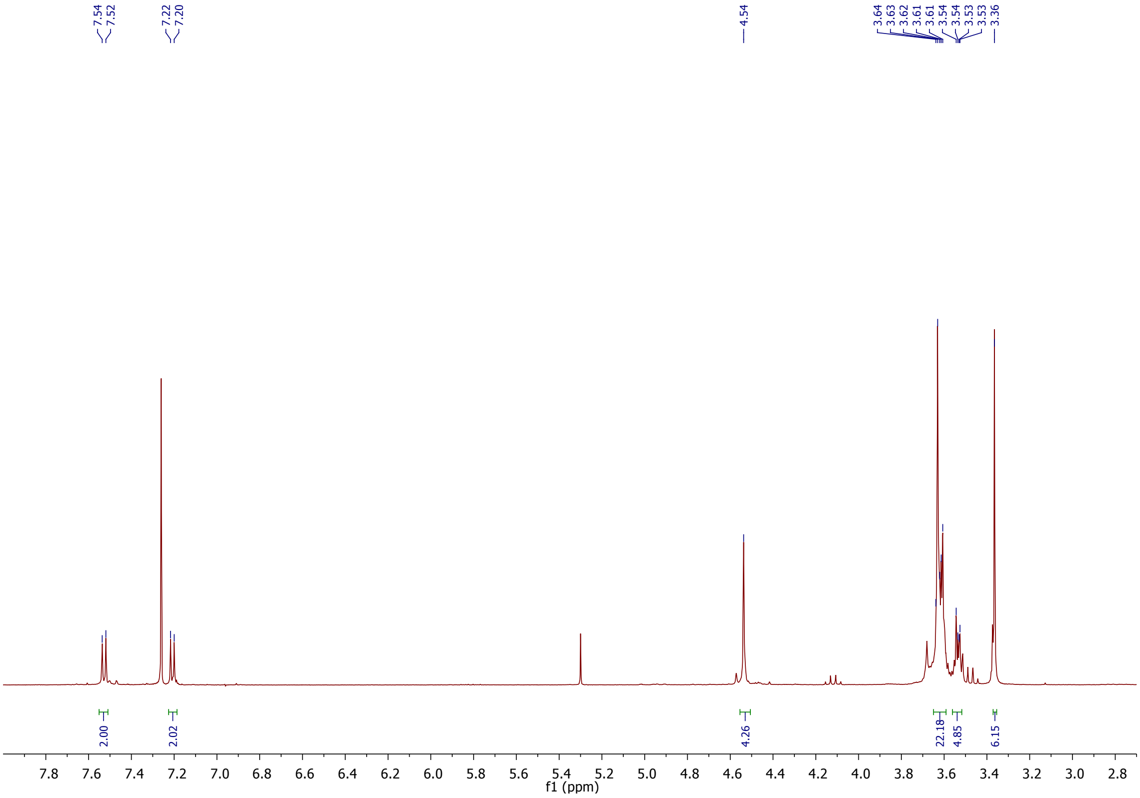
2922.09
2865.09
1675.29
1521.67
1459.55
1417.18
1372.06
1292.18
1248.24
1198.52
1105.30
1029.24
960.12
873.46
698.12
669.83
595.77
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

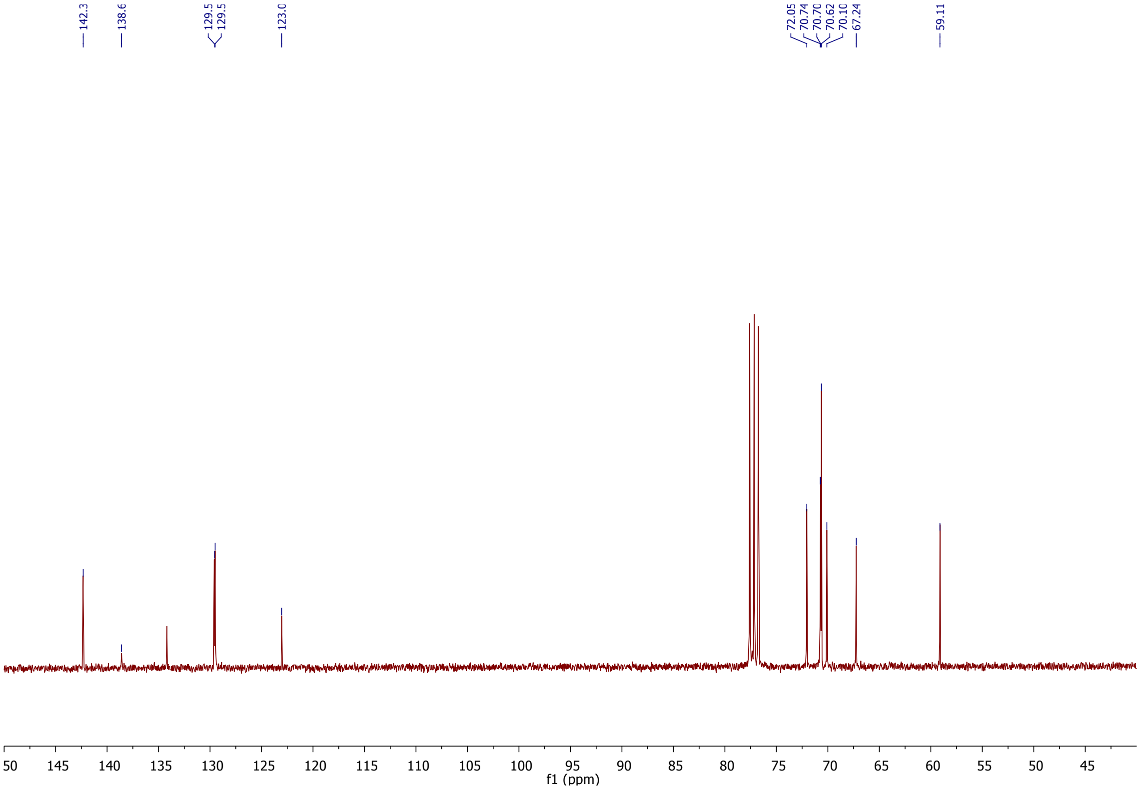
1,1'-(3',4'-dinitro-[2,2':5',2''-terthiophene]-3,3''-diyl)bis(2,5,8,11-tetraoxadodecane) (4)



^{1}H-NMR



^{13}C-NMR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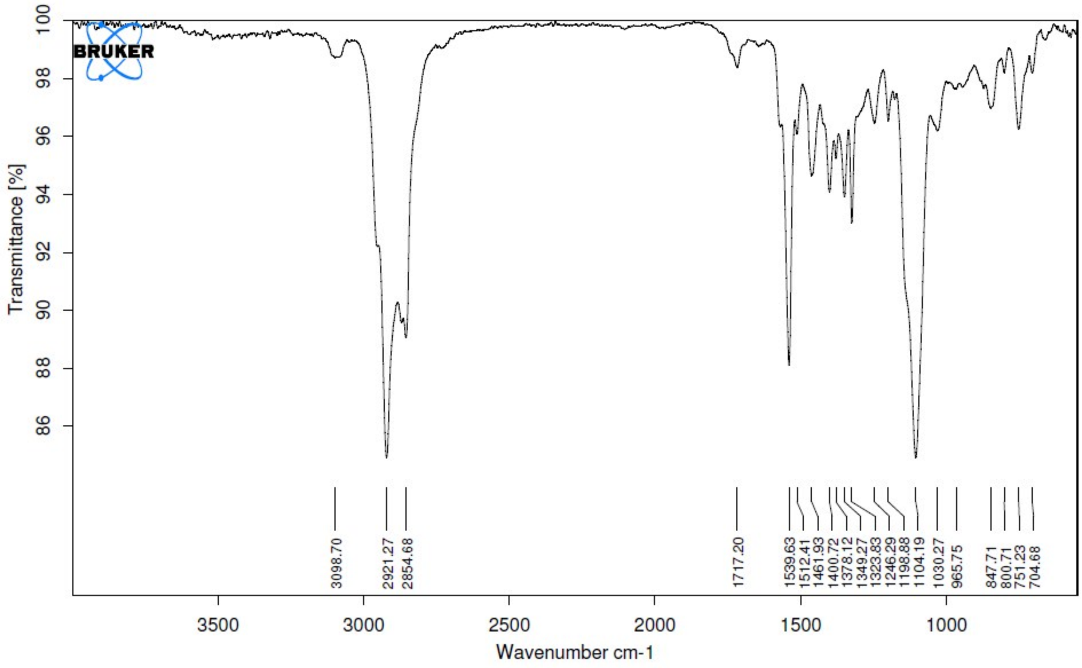
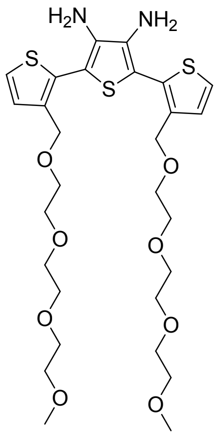
129.5
129.5
123.0
72.05
70.74
70.70
70.62
70.10
67.24
59.11
50
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
f1 (ppm)

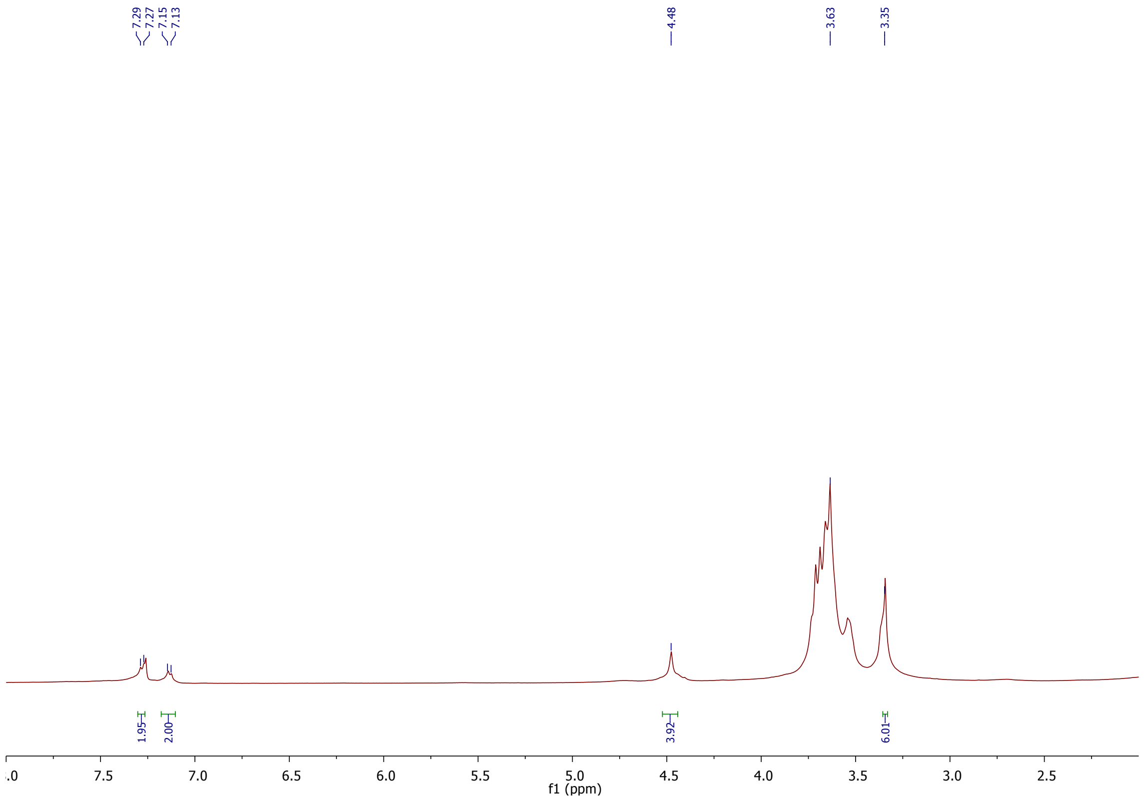
IR


BRUKER
Transmittance [%]
100
98
96
94
92
90
88
86
3098.70
2921.27
2854.68
1717.20
1539.63
1512.41
1461.93
1400.72
1378.12
1349.27
1323.83
1246.29
1198.88
1104.19
1030.27
965.75
847.71
800.71
751.23
704.68
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

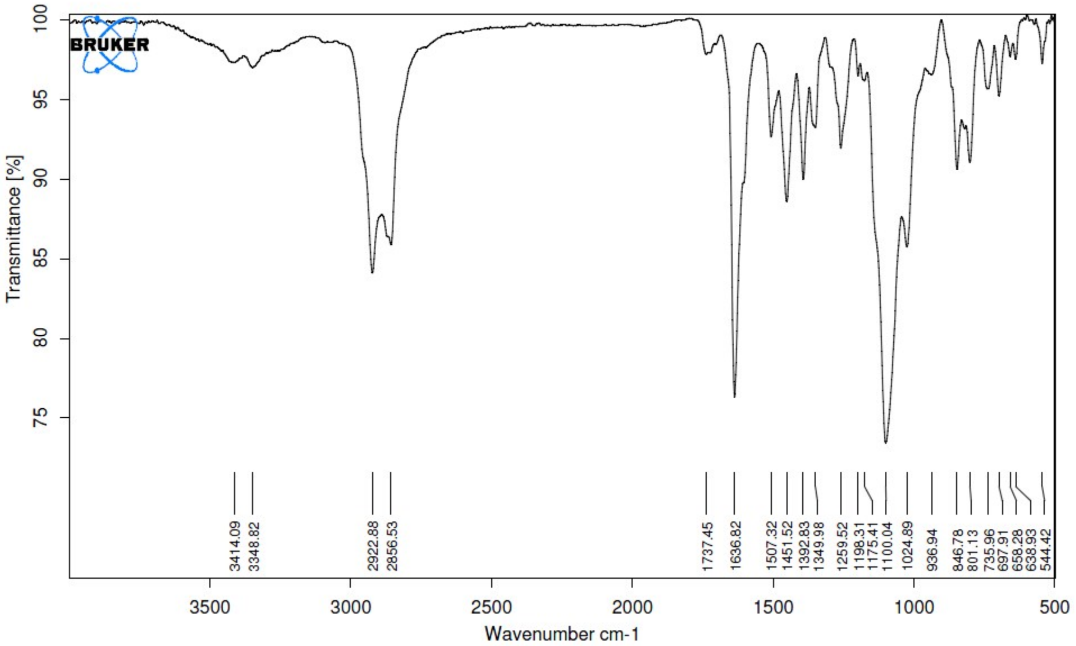
3,3''-di(2,5,8,11-tetraoxadodecyl)-[2,2':5',2''-terthiophene]-3',4'-diamine (5)



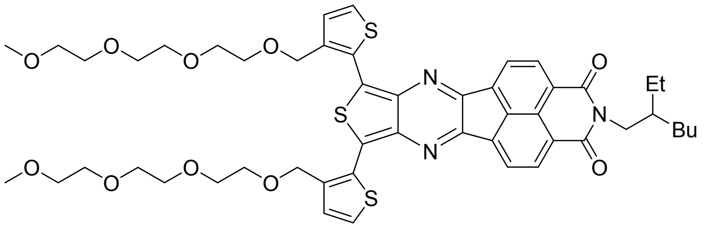
^{1}H-NMR



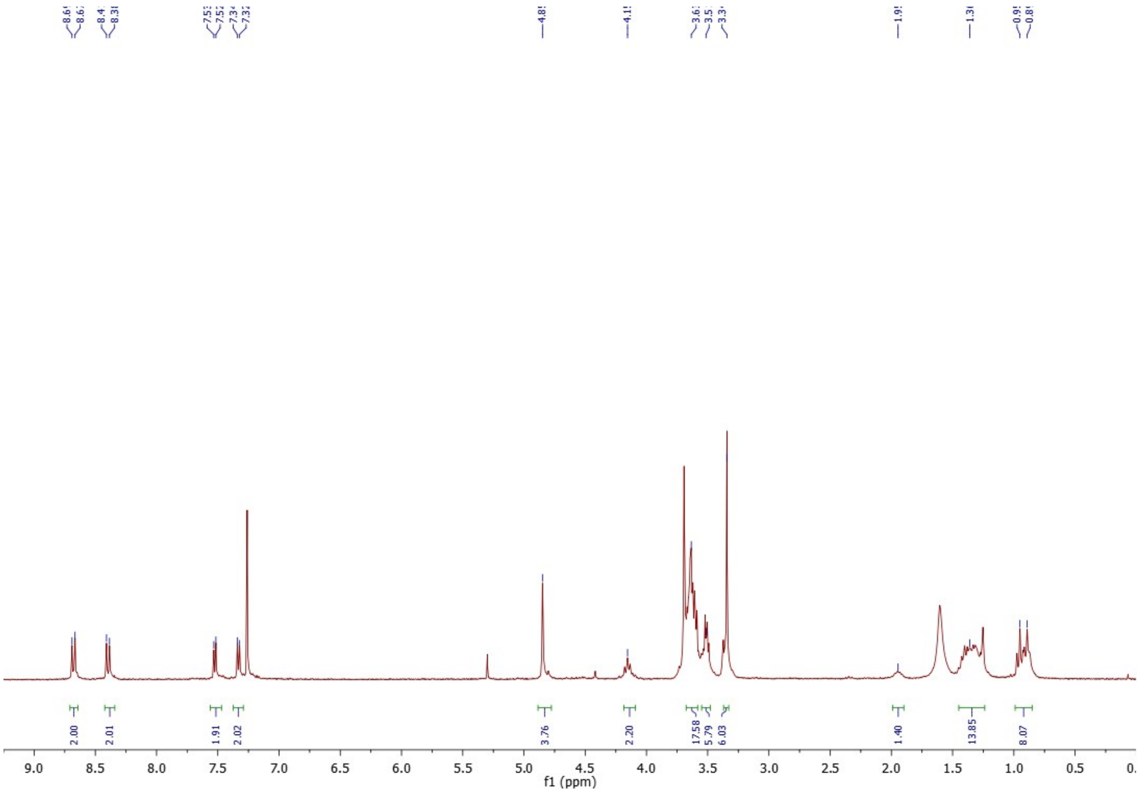
IR



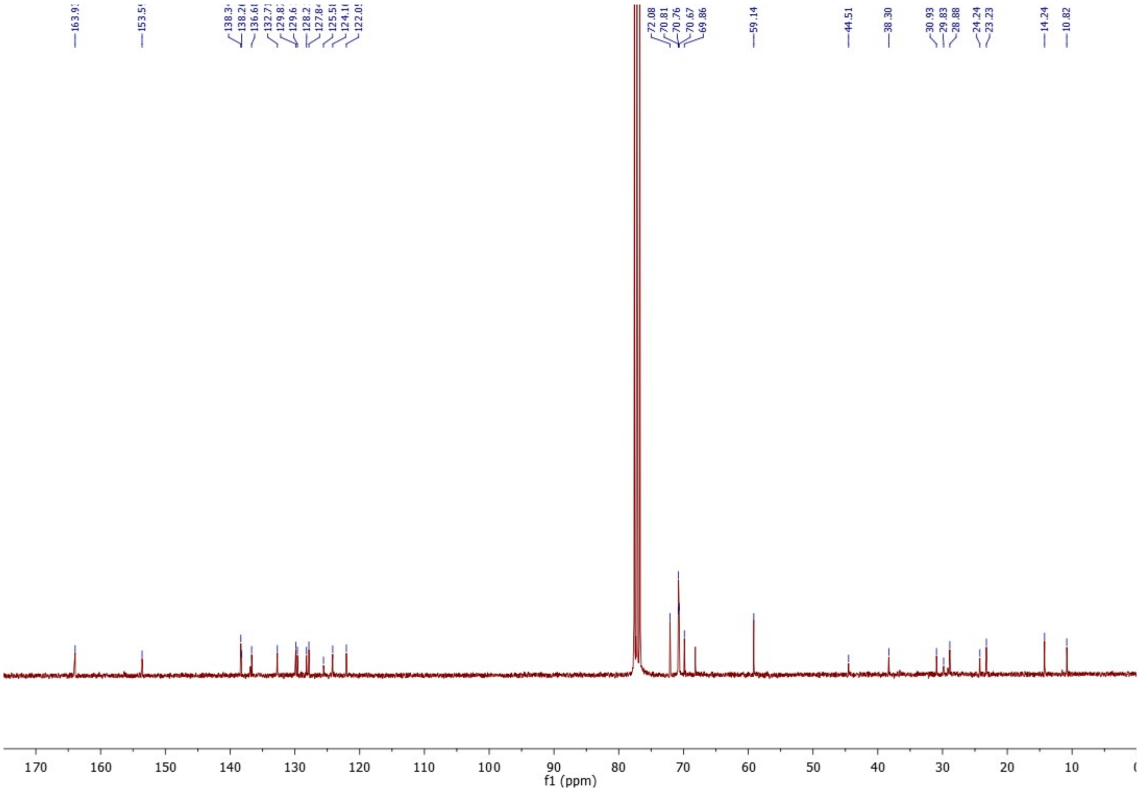
NIP-3T$_{\text{Amphi}}$



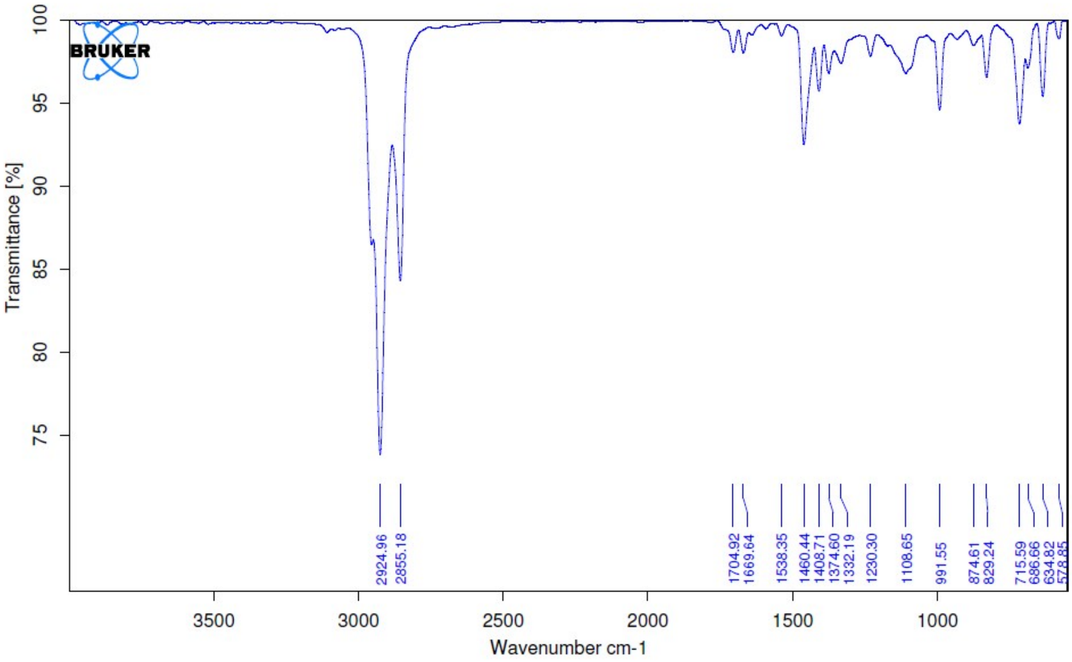
^{1}H-RMN



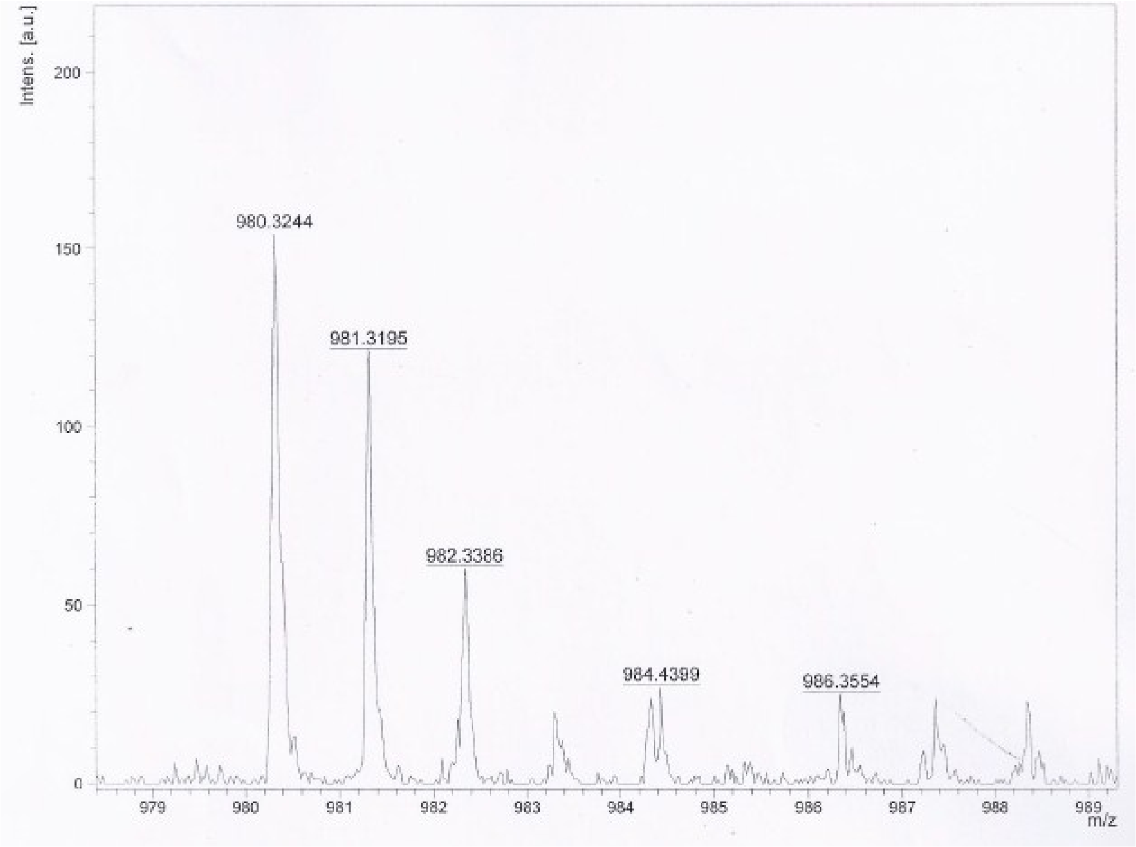
^{13}C-RMN



IR


BRUKER
Transmittance [%]
100
95
90
85
80
75
2924.96
2855.18
1704.92
1669.64
1538.35
1460.44
1408.71
1374.60
1332.19
1230.30
1108.65
991.55
874.61
829.24
715.59
686.66
634.82
578.85
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

MS


Intens. [a.u.]
200
150
100
50
0
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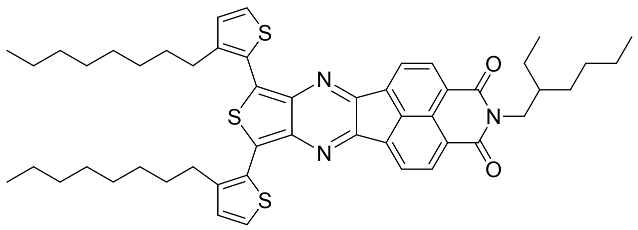
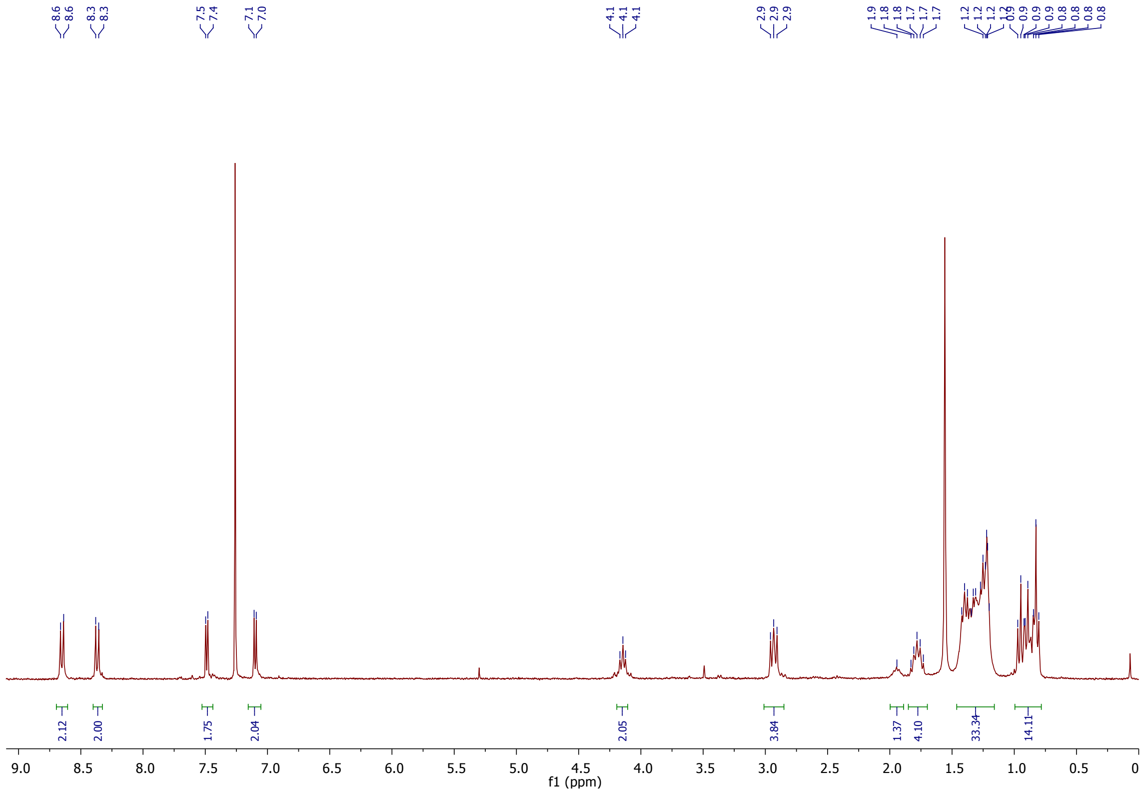
981.3195
982.3386
984.4399
986.3554
979
980
981
982
983
984
985
986
987
988
989
m/z

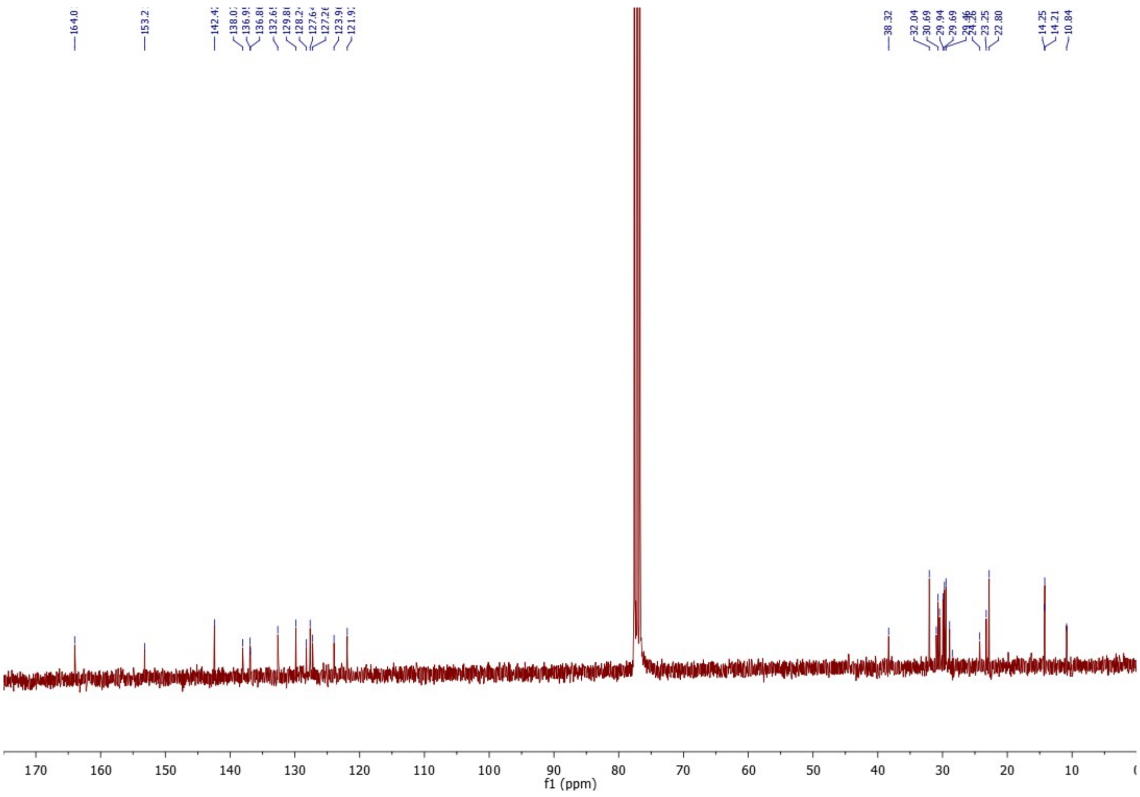
NIP-3T$_{Lipo}$



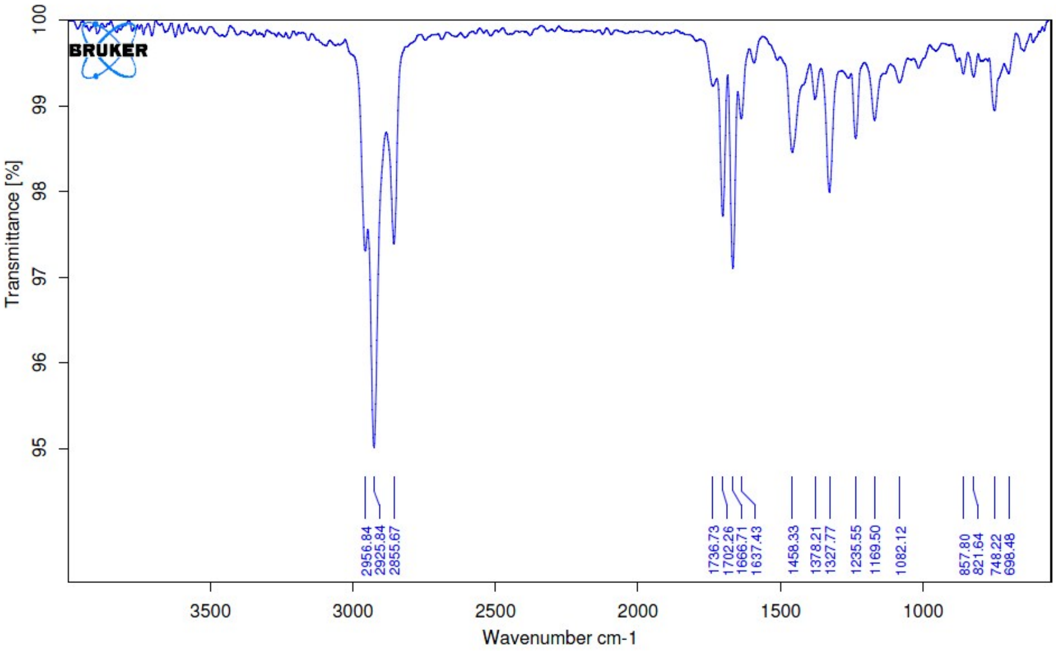
^{1}H-NMR



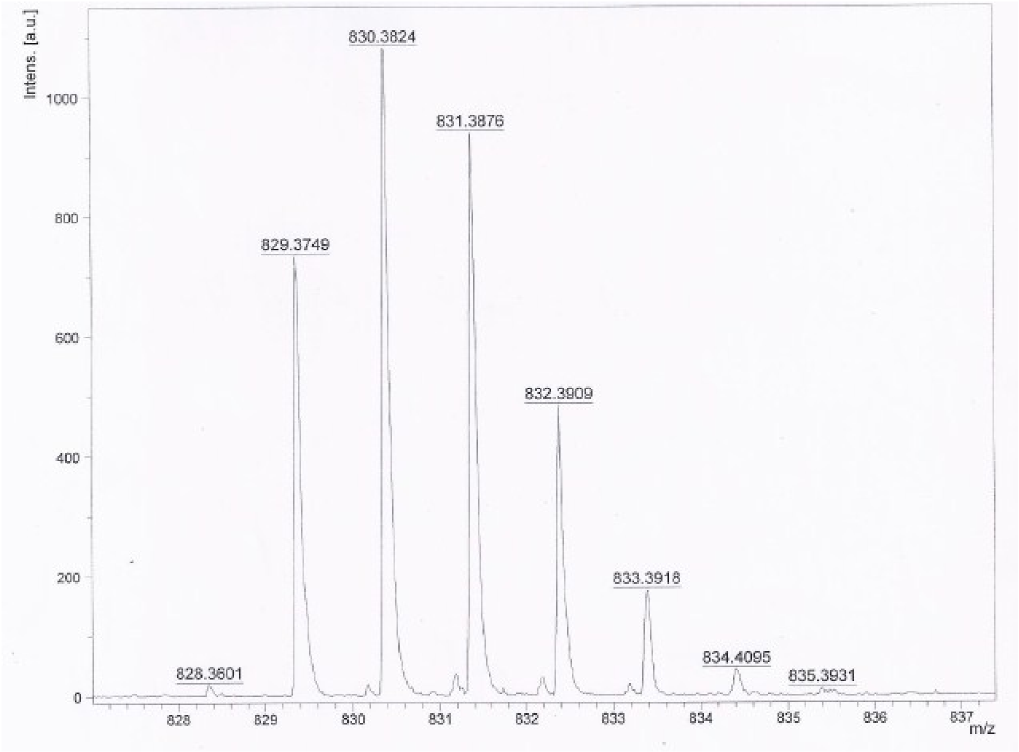
^{13}C-NMR


164.0
153.2
142.4
138.0
136.9
136.8
132.6
129.8
128.2
127.6
127.2
123.9
121.9
38.32
32.04
30.69
29.94
29.69
29.46
24.25
23.25
22.80
14.25
14.21
10.84
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

IR


BRUKER
Transmittance [%]
100
99
98
97
96
95
2956.84
2925.84
2855.67
1736.73
1702.26
1666.71
1637.43
1458.33
1378.21
1327.77
1235.55
1169.50
1082.12
857.80
821.64
748.22
698.48
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

MS


Intens. [a.u.]
1000
800
600
400
200
0
830.3824
831.3876
829.3749
832.3909
833.3918
834.4095
835.3931
828.3601
828
829
830
831
832
833
834
835
836
837
m/z

3.2. Thermogravimetric analysis

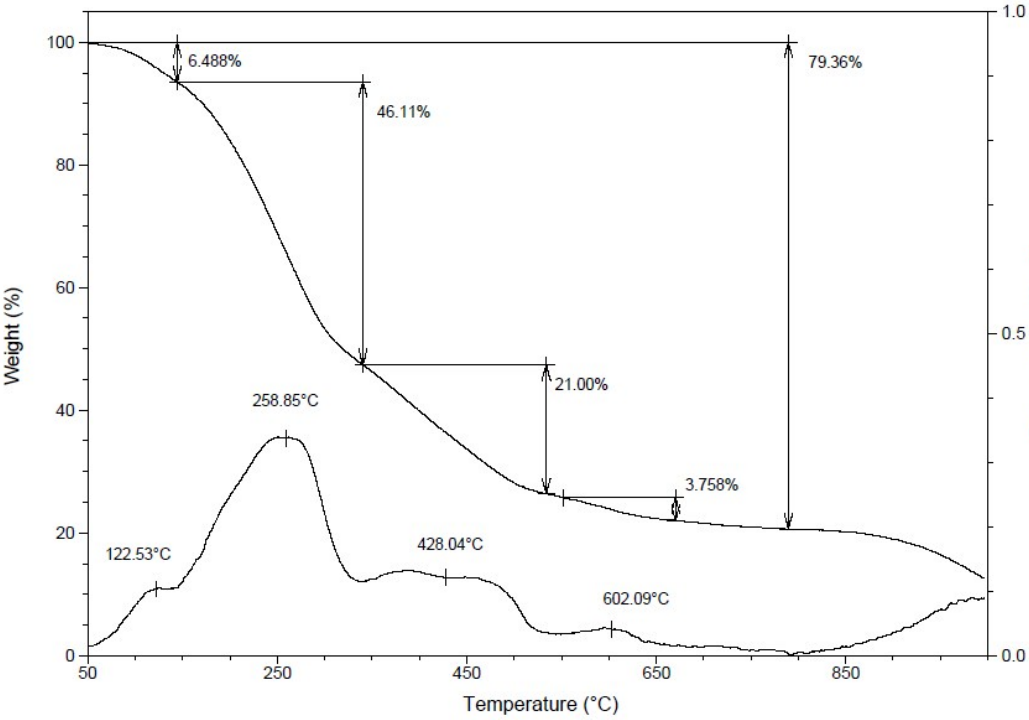


Figure S1. Thermal stability of **NIP-3T$_{\mathbf{Amphi}}$** by thermogravimetric analysis (TGA) in nitrogen gas at a heating of 10ºC/min.

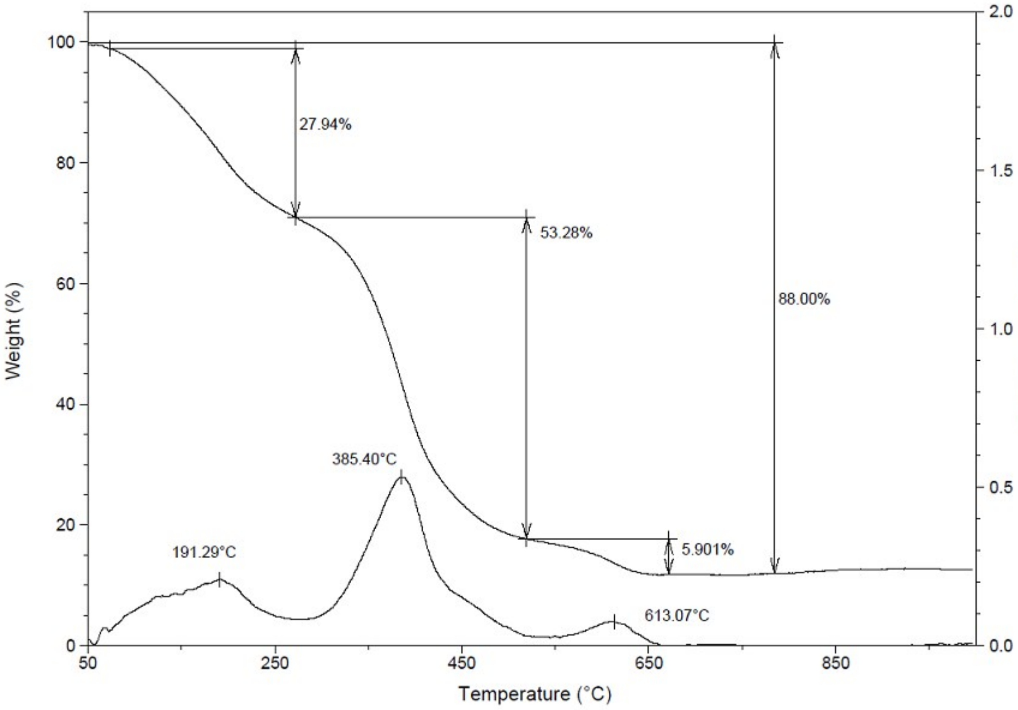


Figure S2. Thermal stability of **NIP-3T$_{\mathbf{Lipo}}$** by thermogravimetric analysis (TGA) in nitrogen gas at a heating of 10ºC/min.

3.3. Molecular Orbitals DFT calculations

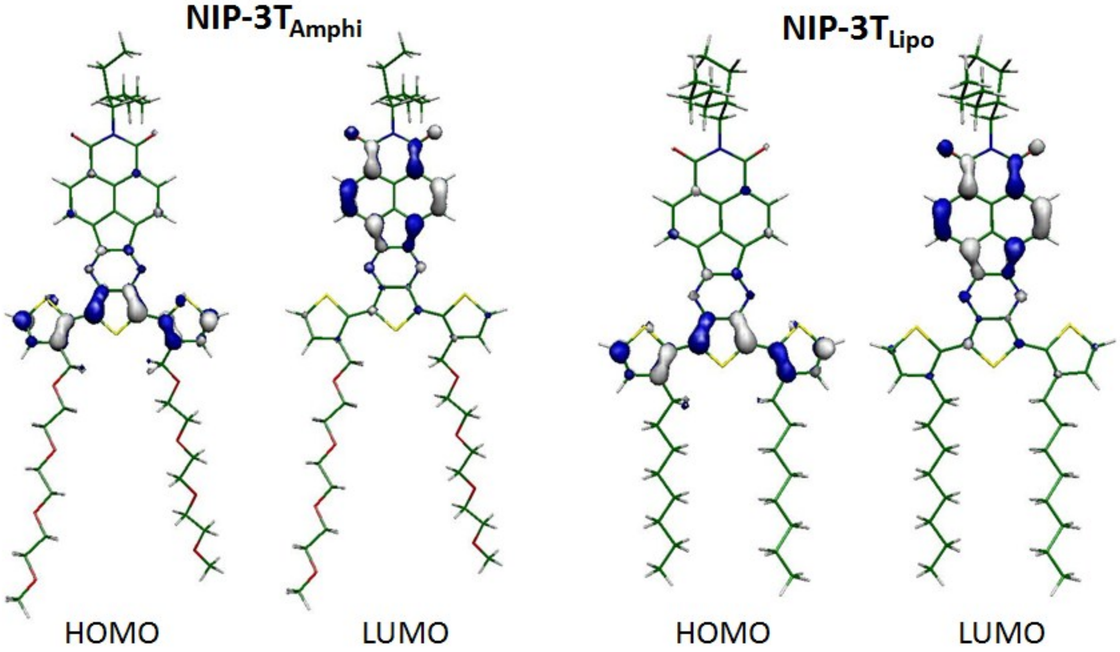


Figure S3. DFT/B3LYP/6-31G** molecular orbital topologies.

3.4. Concentration dependent electronic absorption.

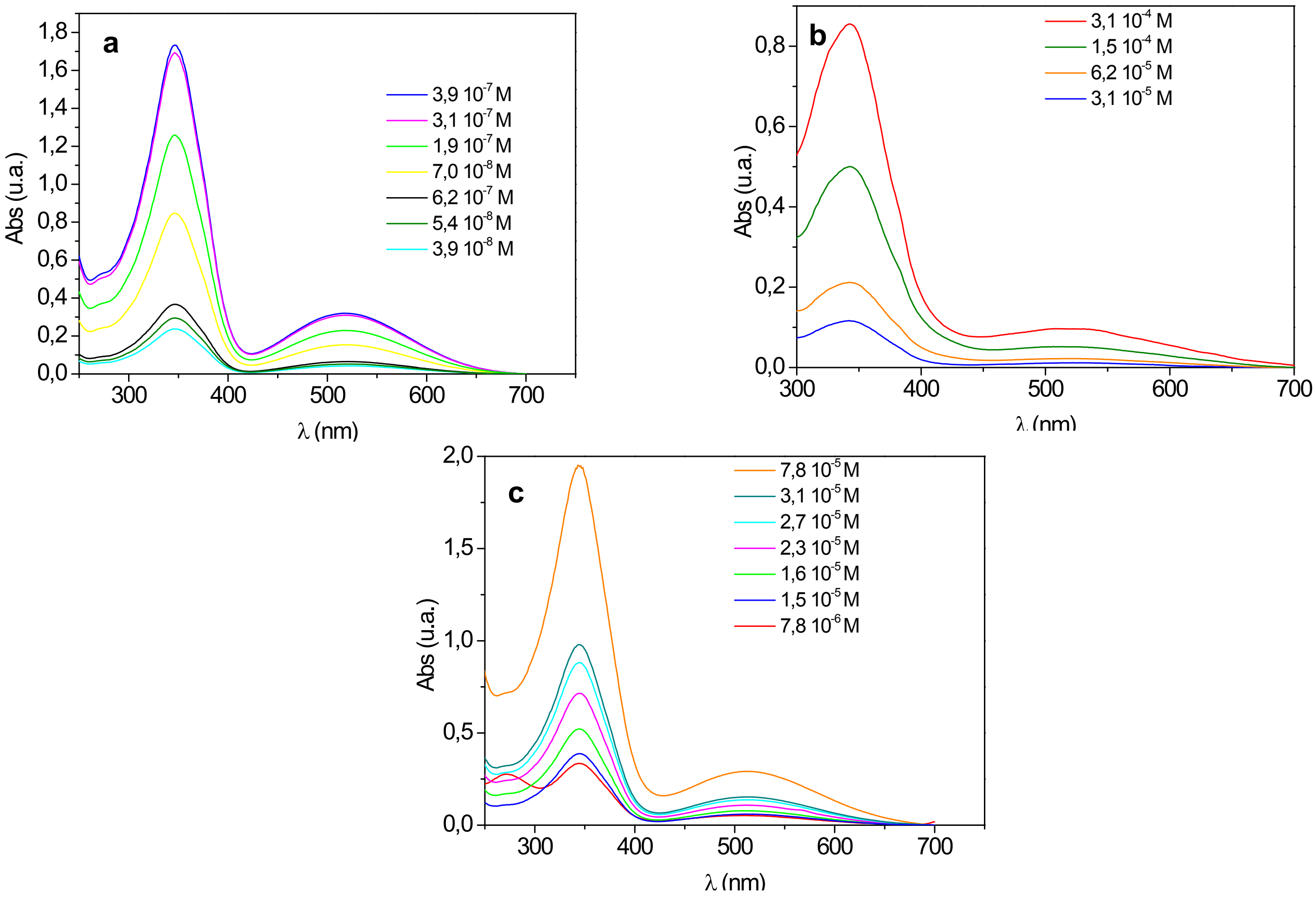


Figure S4.UV-Vis spectra of **NIP-3T$_{\mathbf{Amphi}}$** at different concentrations in a)Dichloromethane, b) Hexane and c) Methanol.

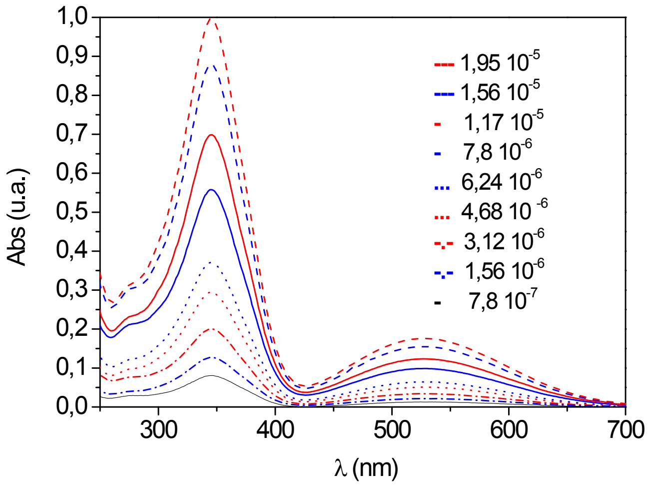


Figure S5.UV-Vis spectra of **NIP-3T$_{\mathbf{Lipo}}$** at different concentrations in dichloromethane.

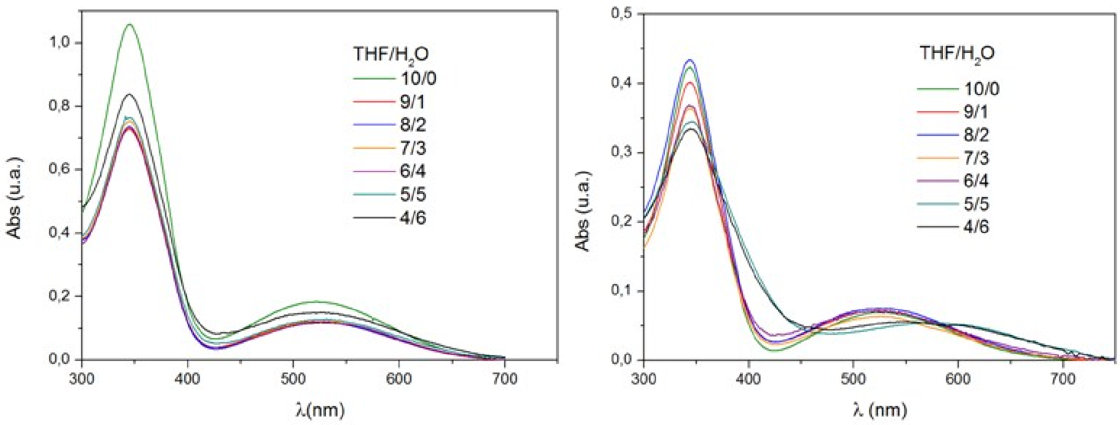


Figure S6.UV-Vis spectra of left) **NIP-3T$_{\mathbf{Amphi}}$** and right) **NIP-3T$_{\mathbf{Lipo}}$** at different mixtures of THF/H_2O.

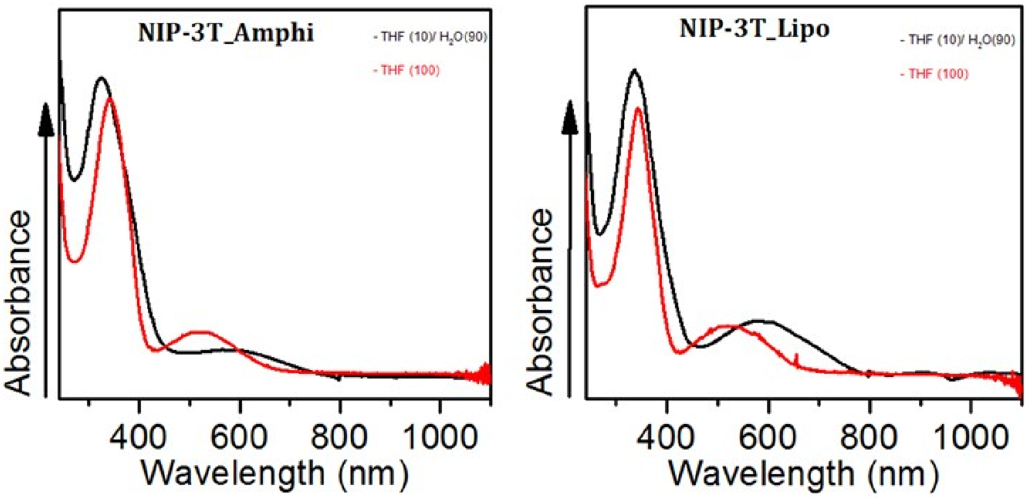


Figure S7.UV-Vis spectra of left) **NIP-3T$_{\mathbf{Amphi}}$** and right) **NIP-3T$_{\mathbf{Lipo}}$** at two extrememixtures of THF/H_2O (10/90 and 100/0).

3.5. Differential scanning calorimetry (DSC analysis)

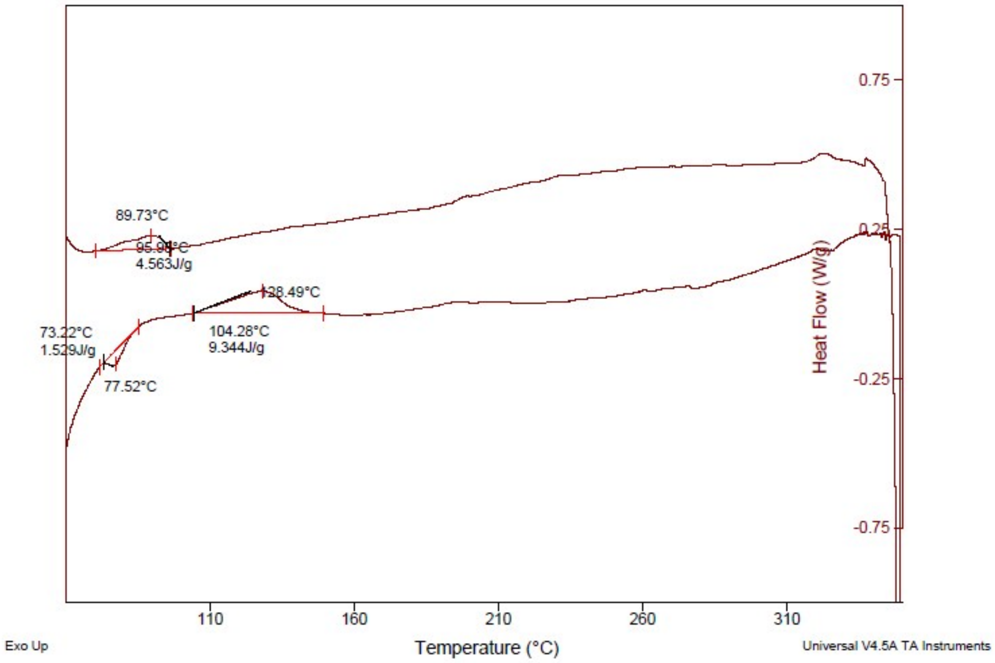


Figure S8. Differential Scanning calorimetry (DSC) curve of compound **NIP-3T$_{\mathbf{Amphi}}$**at a heating rate of 10ºC/min.

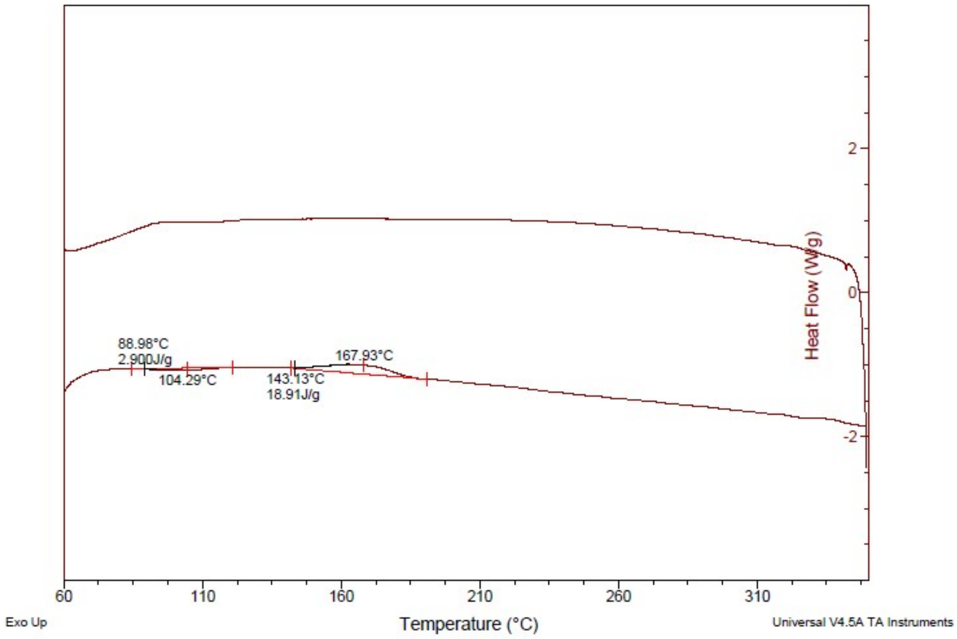
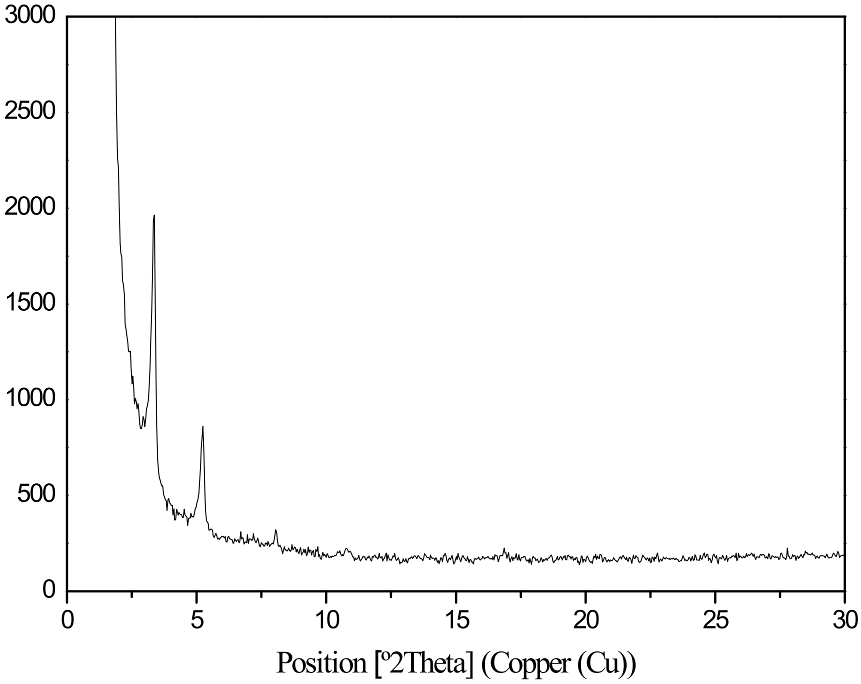


Figure S9. Differential Scanning calorimetry (DSC) curve of compound **NIP-3T$_{\mathbf{Lipo}}$**at a heating rate of 10ºC/min.

3.6. Powder and thin film XRD analysis

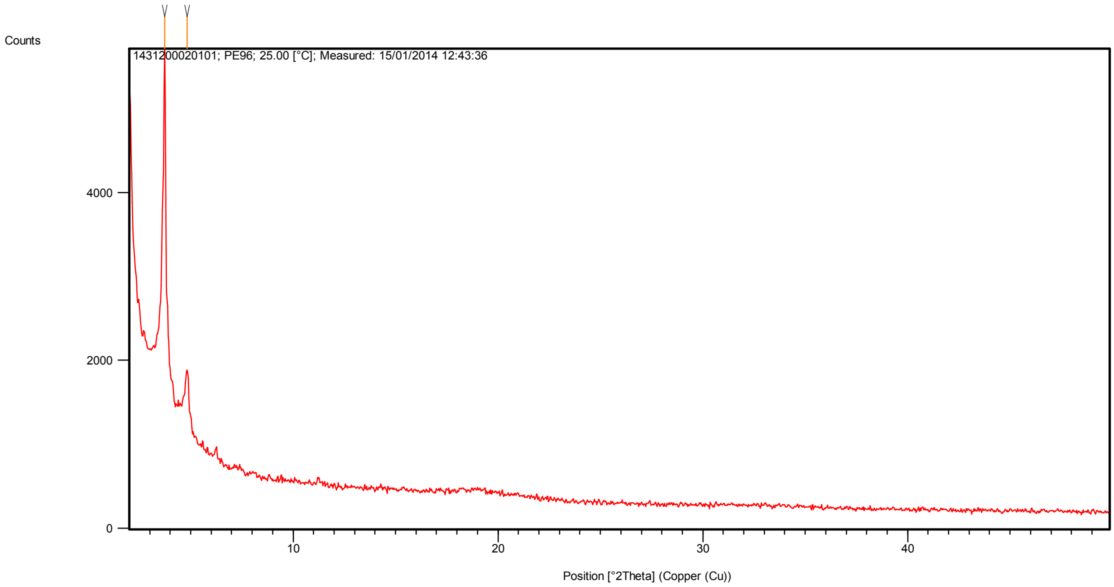
The powder X-ray diffraction (XRD) analysis for **NIP-3T$_{\mathbf{Lipo}}$** showed two peaks corresponding to d-spacingsof 23.71 and 18.29while **NIP-3T$_{\mathbf{Amphi}}$** showed a set of four distinct peaks with d-spacings of 26.33, 16.88, 10.97 and 8.16 Å thus reflecting the more ordered structure of the amphiphilic derivative (Figure S13).



Peak List:

Pos. [°2Th.]	Height [cts]	d-spacing [Å]	Rel. Int. [%]
3.3546	1357.78	26.33826	100.00
5.2347	529.68	16.88224	39.01
8.0581	34.91	10.97233	2.57
10.8335	41.58	8.16680	3.06

Figure S10. Powder X-ray diffraction of **NIP-3T$_{\mathbf{Amphi}}$**.



Peak list:

Pos. [°2Th.]	Height [cts]	d-spacing [Å]	Rel. Int. [%]
3.7258	4044.60	23.71550	100.00
4.8315	670.66	18.29014	16.58

Figure S11. Powder X-ray diffraction of **NIP-3T**$_{\mathbf{Lipo}}$.

Thin film XRD analysis

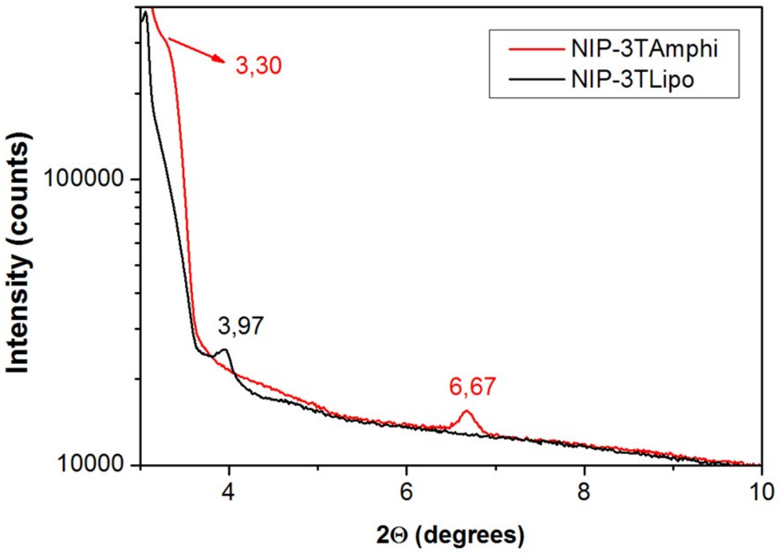


Figure S12. Thin film X-ray diffraction of **NIP-3T$_{\mathbf{Amphi}}$** and **NIP-3T$_{\mathbf{Lipo}}$**.

3.7. M062X estimated dimers for **NIP-3T$_{\mathbf{Amphi}}$** and **NIP-3T$_{\mathbf{Lipo}}$**.

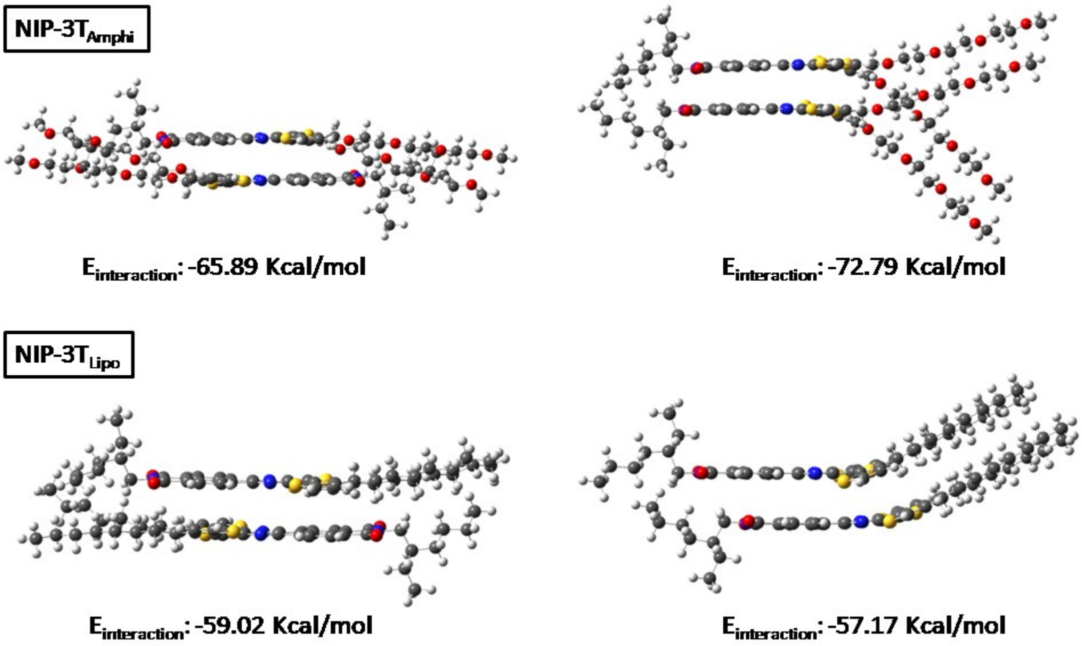


Figure S13.M062X/6-31G** estimated dimers (left: antiparallel configuration (AP) and right: parallel configuration (P)) for **NIP-3T$_{\mathbf{Amphi}}$** and **NIP-3T$_{\mathbf{Lipo}}$**.

3.8. Transfer integral DFT calculation.

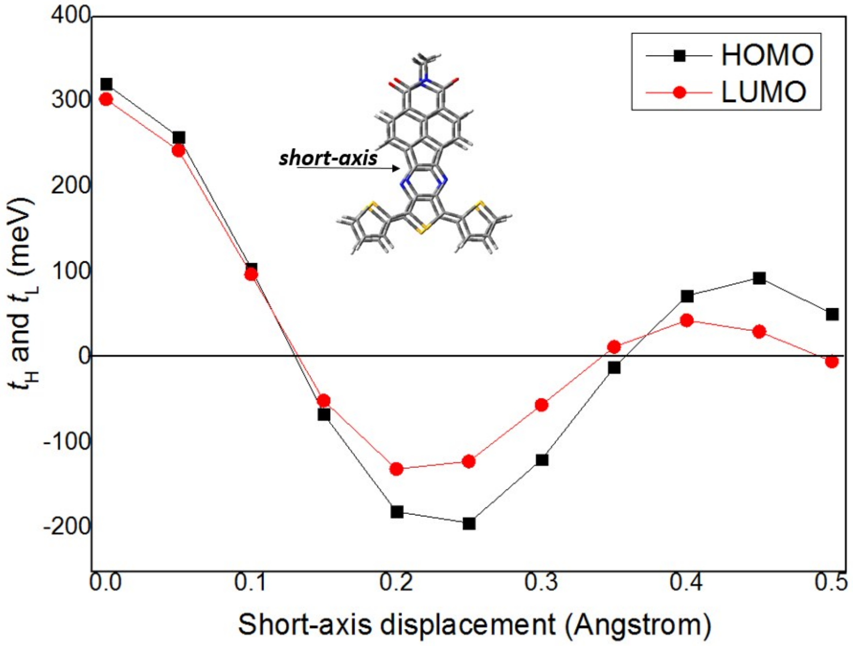


Figure S14. Evolution of the HOMO and LUMO transfer integrals for an unsubstituted naphthalimide-fused thienopyrazine cofacial dimer, as a function of the short-axis displacements of the top molecule. The intermolecular distance is set at 3.50 Å, the average intermolecular separation found in crystals of π-conjugated molecules along the π-stacks.