

Supplementary information

N-heteroheptacenequinone and N-heterononacenequinone: synthesis, physical properties, crystal structures and photoelectrochemical behaviors

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Table S1. Crystal data and structure refinement for **TAHD**.

Identification code	TAHD
Empirical formula	C70 H92 N4 O2 Si4
Formula weight	1133.84
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.1577(4) Å α = 84.169(2)°. b = 10.6488(4) Å β = 88.405(2)°. c = 17.1688(6) Å γ = 63.987(2)°.
Volume	1660.04(11) Å ³
Z	1
Density (calculated)	1.134 Mg/m ³
Absorption coefficient	0.135 mm ⁻¹
F(000)	612
Crystal size	0.40 x 0.24 x 0.02 mm ³
Theta range for data collection	2.34 to 30.12°.
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 14, -24 ≤ l ≤ 24
Reflections collected	58385
Independent reflections	9733 [R(int) = 0.0822]
Completeness to theta = 30.12°	99.5 %
Max. and min. transmission	0.9973 and 0.9479
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9733 / 6 / 374
Goodness-of-fit on F ²	1.040
Final R indices [I > 2sigma(I)]	R1 = 0.0772, wR2 = 0.1969
R indices (all data)	R1 = 0.1538, wR2 = 0.2499
Largest diff. peak and hole	1.058 and -0.465 e.Å ⁻³

Table S2. Crystal data and structure refinement for **TAND**.

Identification code	TAND
Empirical formula	C ₈₂ H ₁₀₂ N ₆ O ₂ Si ₄
Formula weight	1316.06
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.9319(8) Å α = 110.316(3)°. b = 14.4277(12) Å β = 97.166(3)°. c = 18.4216(16) Å γ = 101.674(3)°.
Volume	1892.0(3) Å ³
Z	1
Density (calculated)	1.155 Mg/m ³
Absorption coefficient	0.128 mm ⁻¹
F(000)	708
Crystal size	0.22 x 0.20 x 0.02 mm ³
Theta range for data collection	1.56 to 27.91°.
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 19, -24 ≤ l ≤ 24
Reflections collected	30885
Independent reflections	9032 [R(int) = 0.1013]
Completeness to theta = 27.91°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0 and 0.84
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9032 / 0 / 437
Goodness-of-fit on F ²	0.993
Final R indices [I > 2σ(I)]	R1 = 0.0611, wR2 = 0.1056
R indices (all data)	R1 = 0.1398, wR2 = 0.1346
Largest diff. peak and hole	0.391 and -0.444 e.Å ⁻³

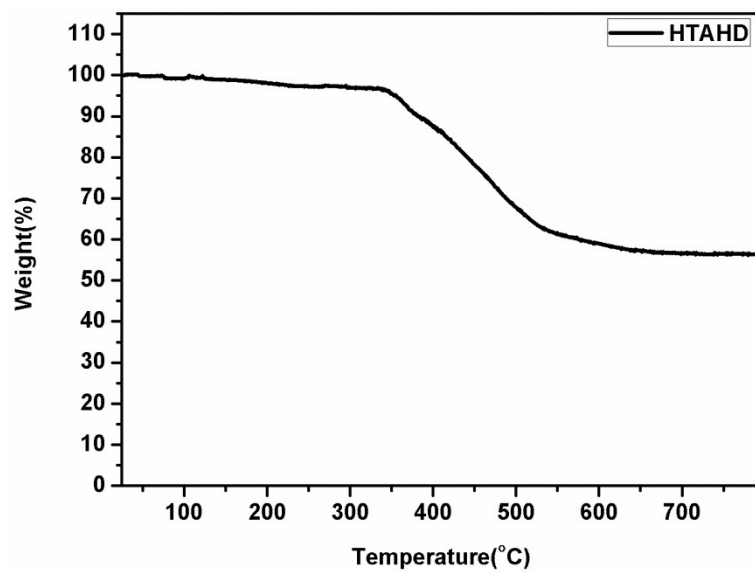


Figure S1. The TGA curve of HTAHD.

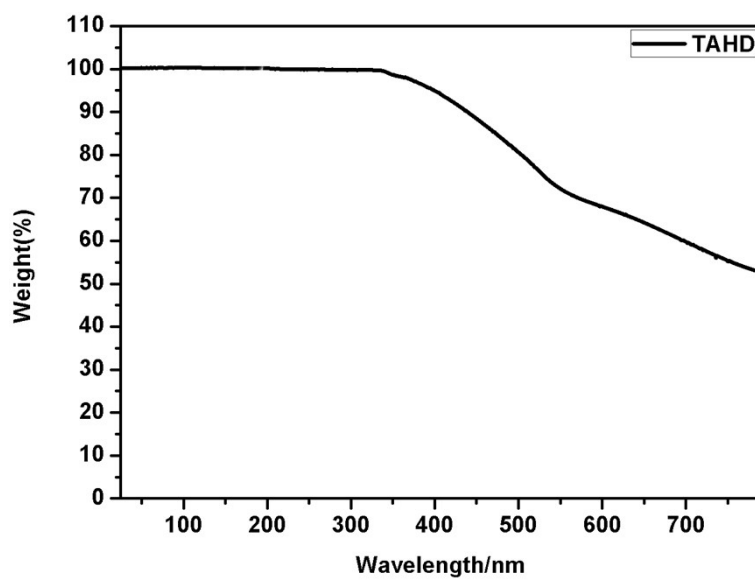


Figure S2. The TGA curve of TAHD.

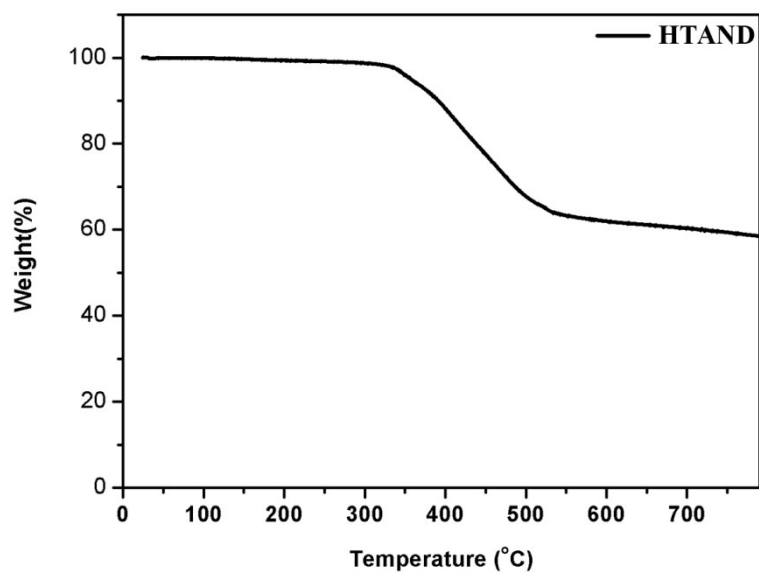


Figure S3. The TGA curve of HTAND.

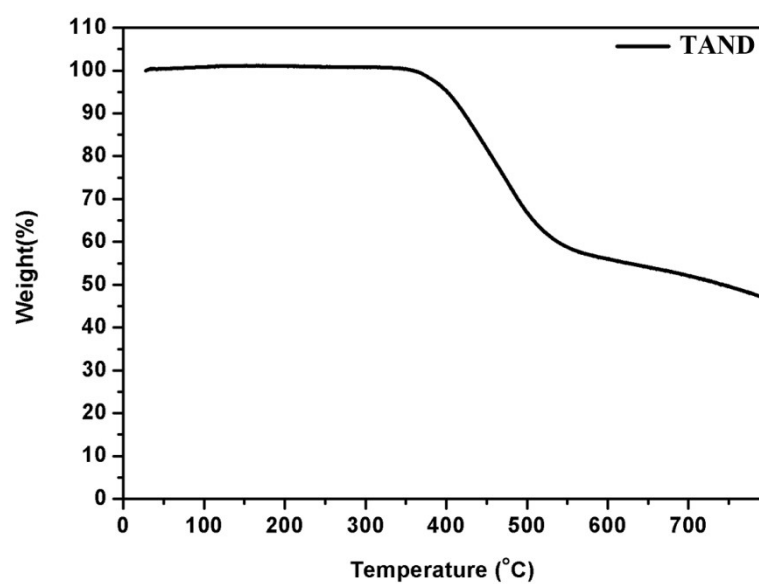


Figure S4. The TGA curve of TAND.

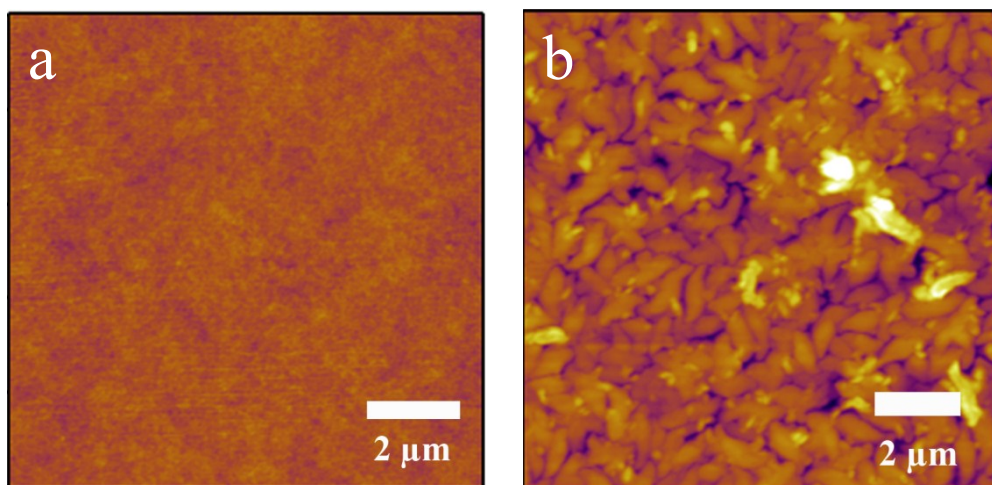


Figure S5. AFM images of (a) TAHD and (b) TAND thin films by spin-coating

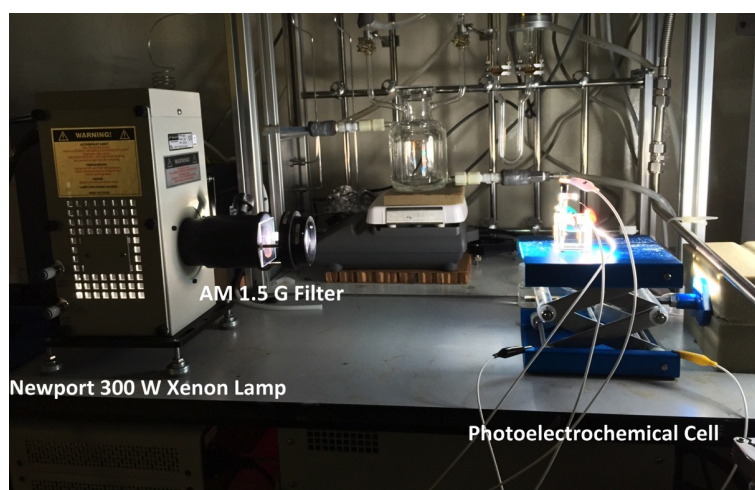


Figure S6. Experimental set-up for photoelectrochemical tests.

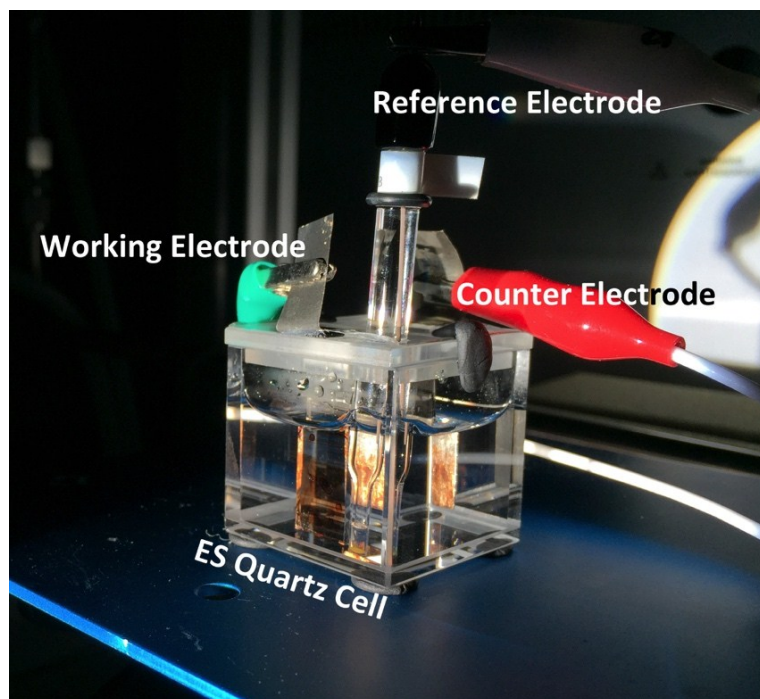


Figure S7. Photoelectrochemical cell (three electrode set-up) applied in this work.

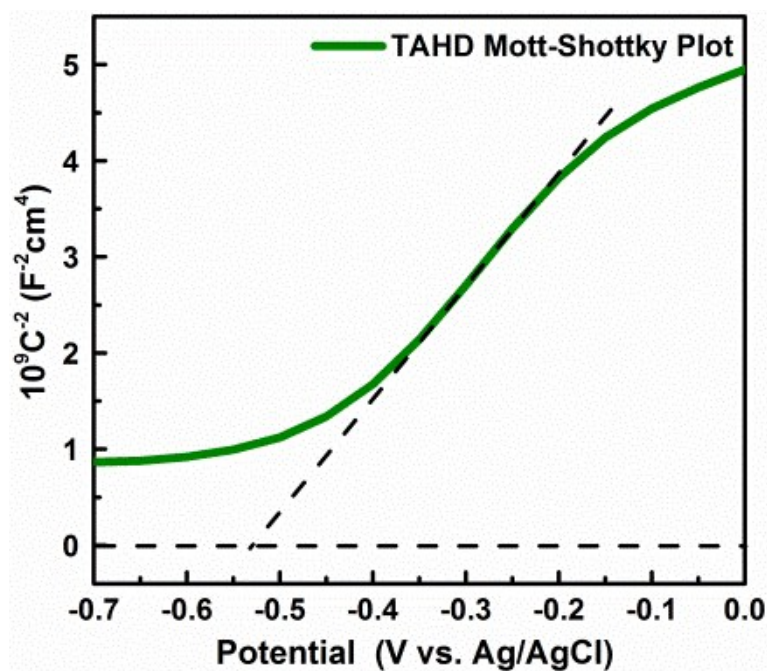


Figure S8. Mott-Schottky plot of **TAHD** measured at a frequency of 1000 Hz. The flat-band potential of **TAHD** is indicated by the intercept of the dashed lines.

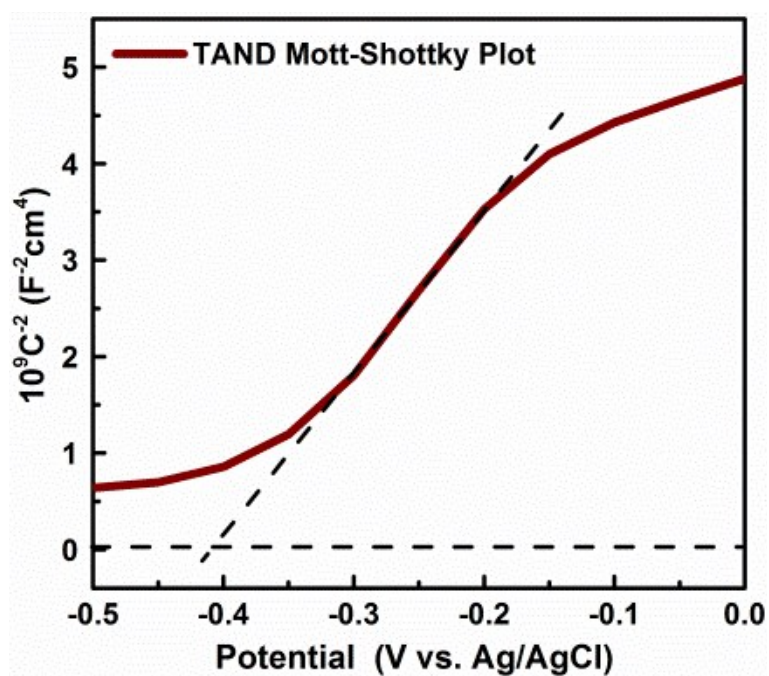


Figure S9. Mott-Schottky plot of **TAND** measured at a frequency of 1000 Hz. The flat-band potential of **TAND** is indicated by the intercept of the dashed lines.

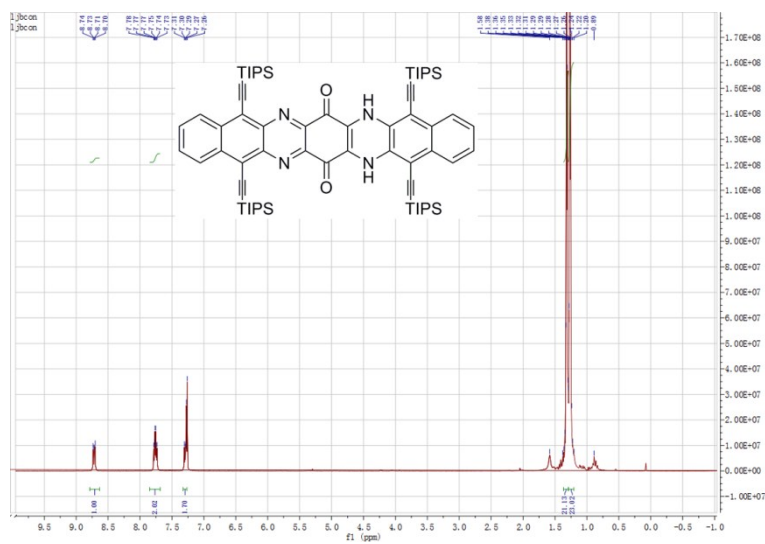


Figure S10. The ^1H NMR of compound HTAHD.

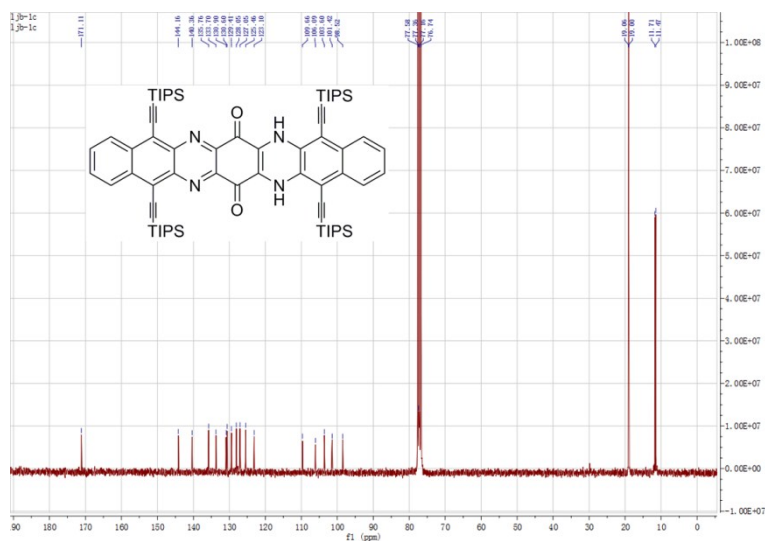


Figure S11. The ^{13}C NMR of compound HTAHD.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

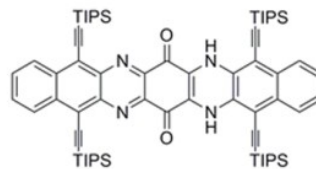
57 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-70 H: 0-95 N: 0-4 O: 0-2 Si: 0-4

C70H94N4O2Si4

LJB-3.3 (0.082) Cm (2.7)



1: TOF MS ES+
3.70e+001

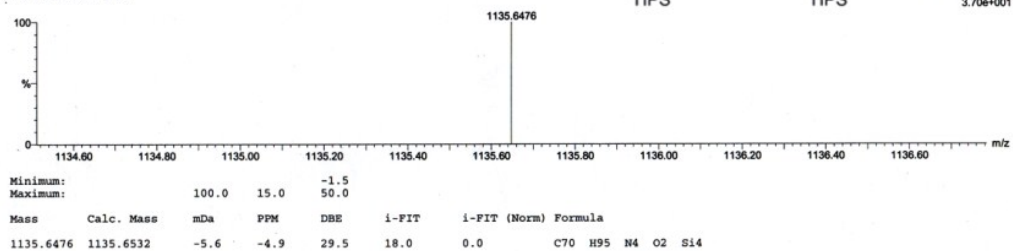


Figure S12. The HRMS of compound HTAHD.

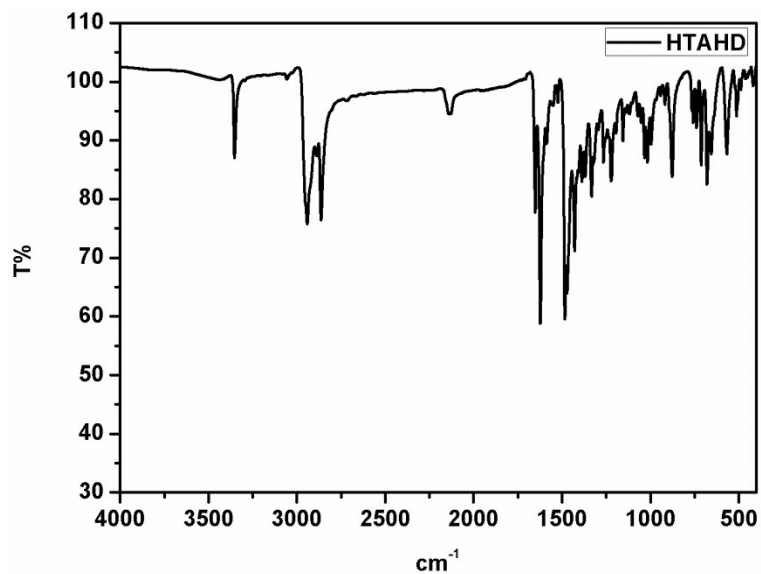


Figure S13. The FTIR of compound HTAHD.

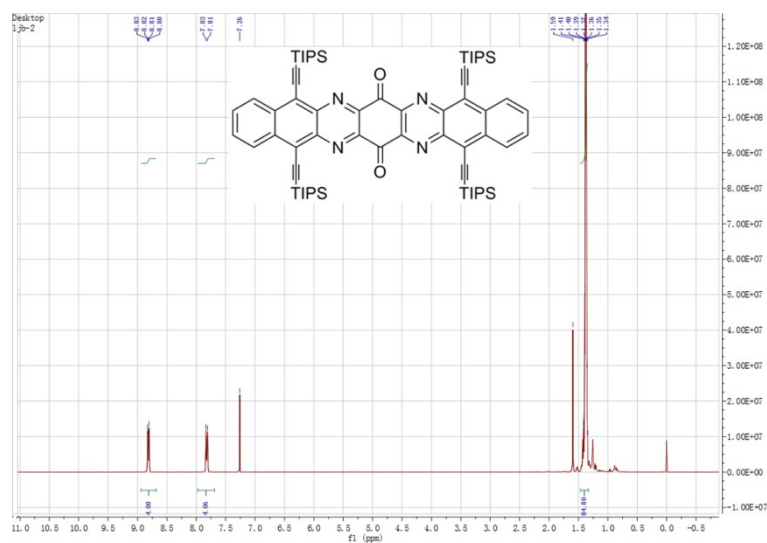


Figure S14. The ^1H NMR of compound TAHD.

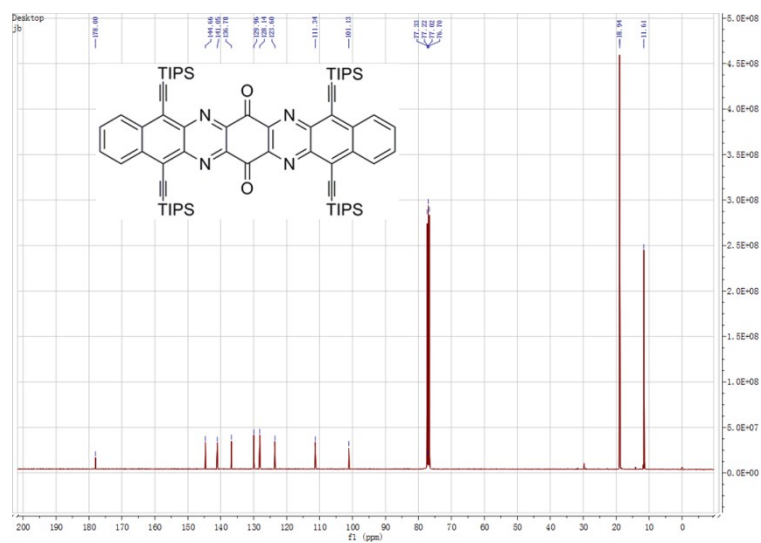


Figure S15. The ^{13}C NMR of compound TAHD.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

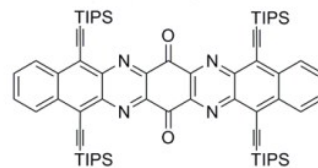
57 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

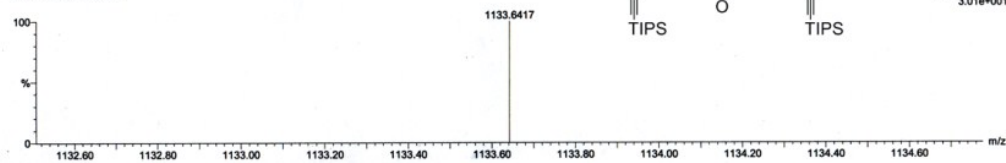
C: 0-70 H: 0-93 N: 0-4 O: 0-2 Si: 0-4

C70H92N4O2Si4

LJB-4.3 (0.083) Cm (1:7)



1: TOF MS ES+
3.01e+001



Minimum:								
Maximum:	100.0	15.0	-1.5	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
1133.6417	1133.6376	4.1	3.6	30.5	17.7	0.0	C70 H93 N4 O2 Si4	

Figure S16. The HRMS of compound TAHD.

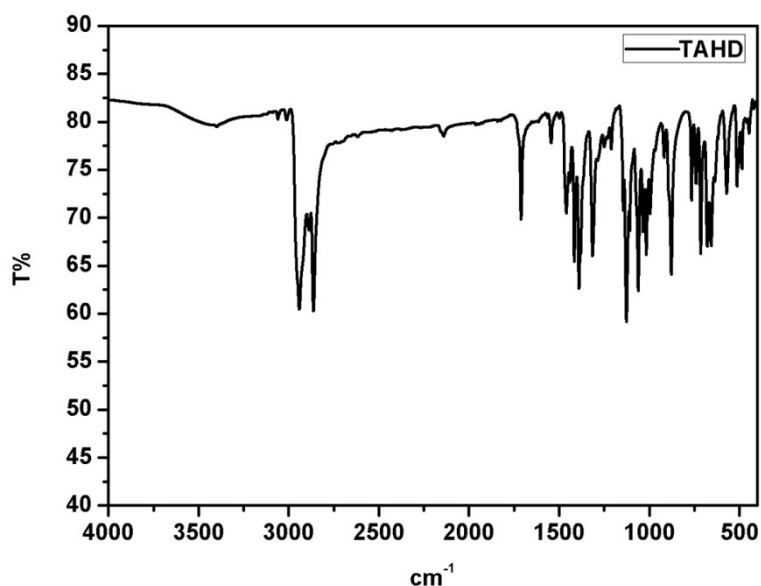


Figure S17. The FTIR of compound TAHD.

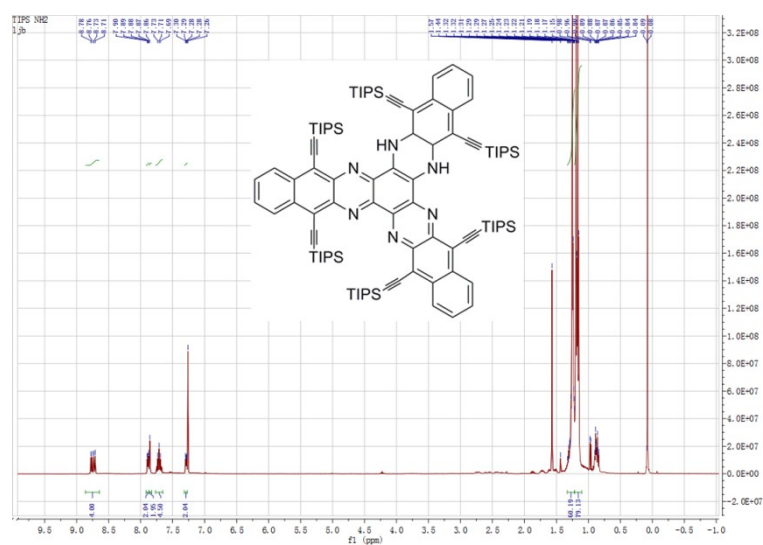


Figure S18. The ^1H NMR of compound **HHATA**.

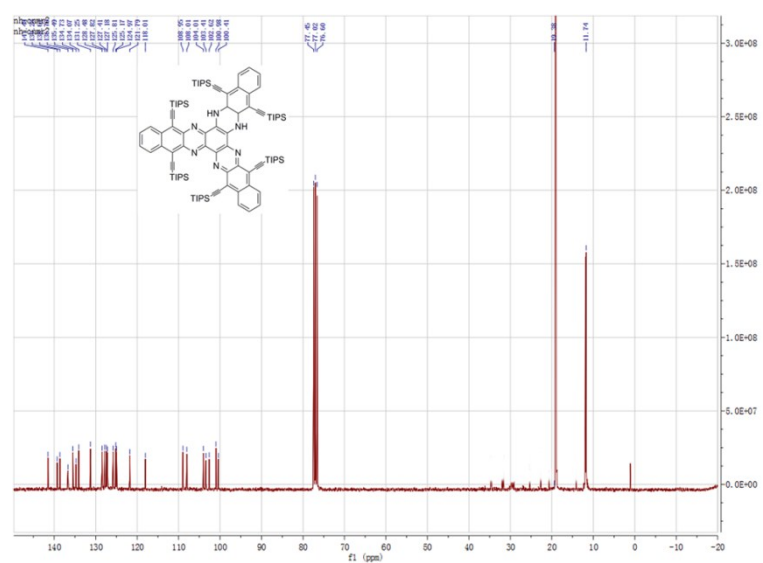


Figure S19. The ^{13}C NMR of compound **HHATA**.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

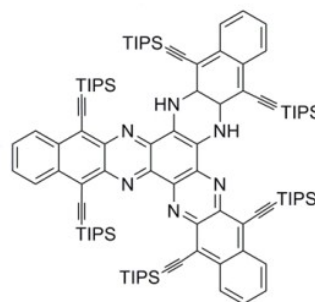
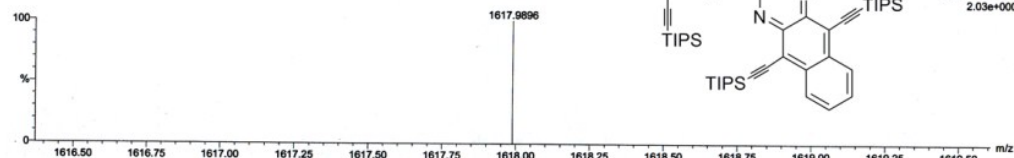
34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-102 H: 0-141 N: 0-6 Si: 0-6

C102H140N6Si6

LJB-1.3 (0.082) Cm (1:16)



1: TOF MS ES+
2.03e+000

Minimum:									
Maximum:	100.0	15.0		-1.5	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
1617.9896	1617.9833	6.3	3.9	41.5	13.3	0.0	C102 H141 N6 Si6		

Figure S20. The HRMS of compound HHATA.

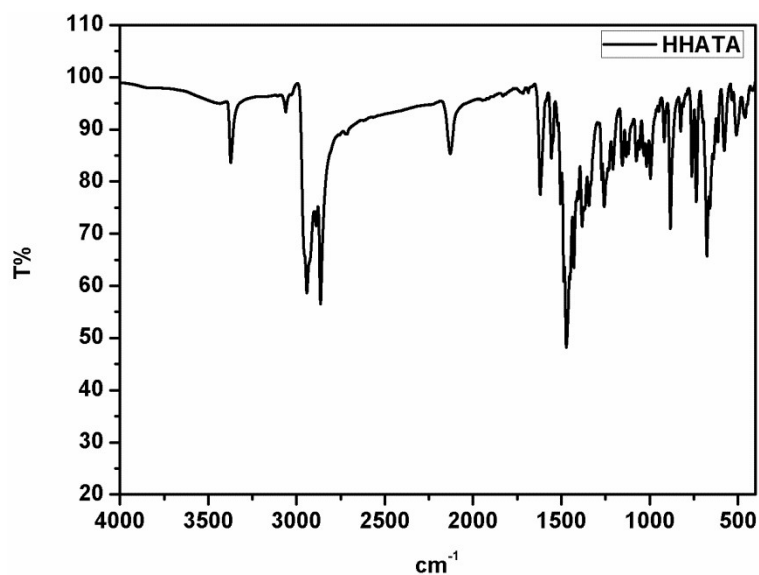


Figure S21. The FTIR of compound HHATA.

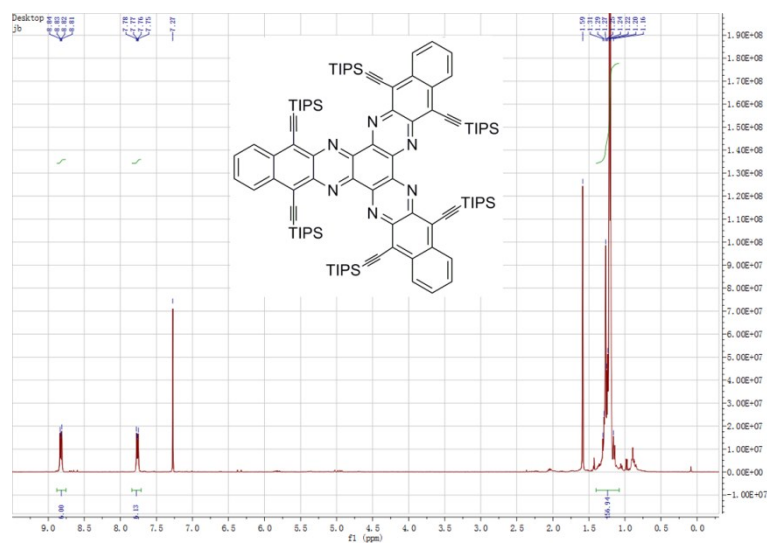


Figure S22. The ^1H NMR of compound HATA.

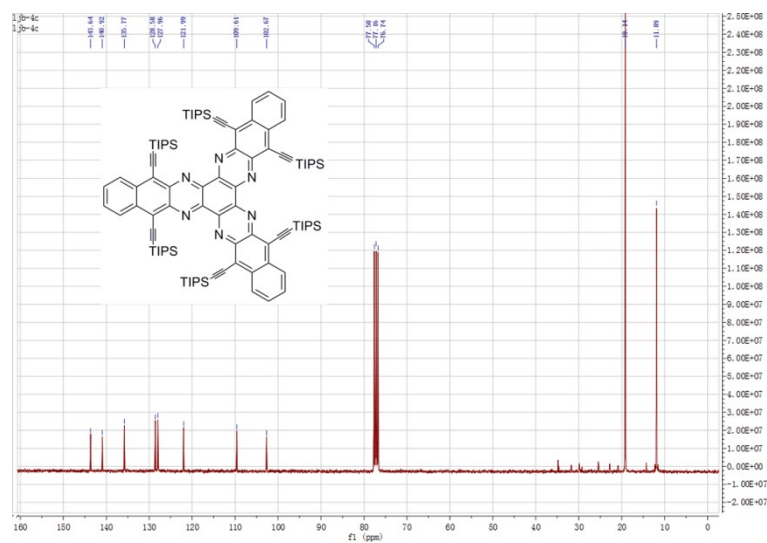


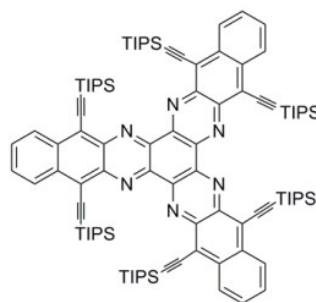
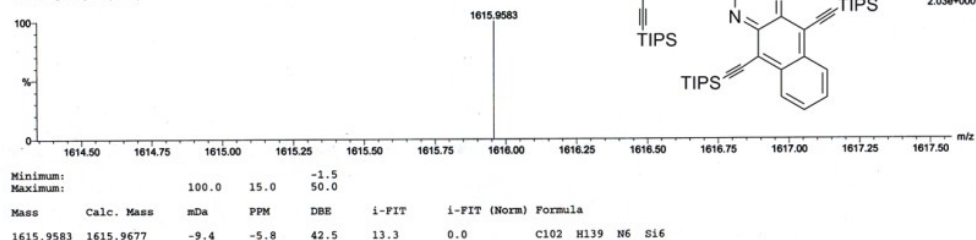
Figure S23. The ^{13}C NMR of compound HATA.

Elemental Composition Report

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
 34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
 Elements Used:
 C: 0-102 H: 0-140 N: 0-6 S: 0-6
 C102H138N6S6
 LJB-2 17 (0.397) Cm (15.22)



1: TOF MS ES+
2.03e+000

Figure S24. The HRMS of compound **HATA**.

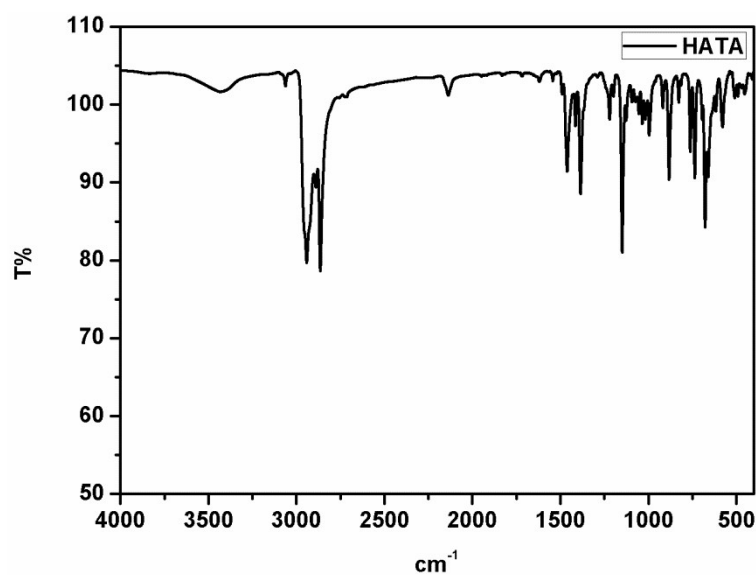


Figure S25. The FTIR of compound **HATA**.

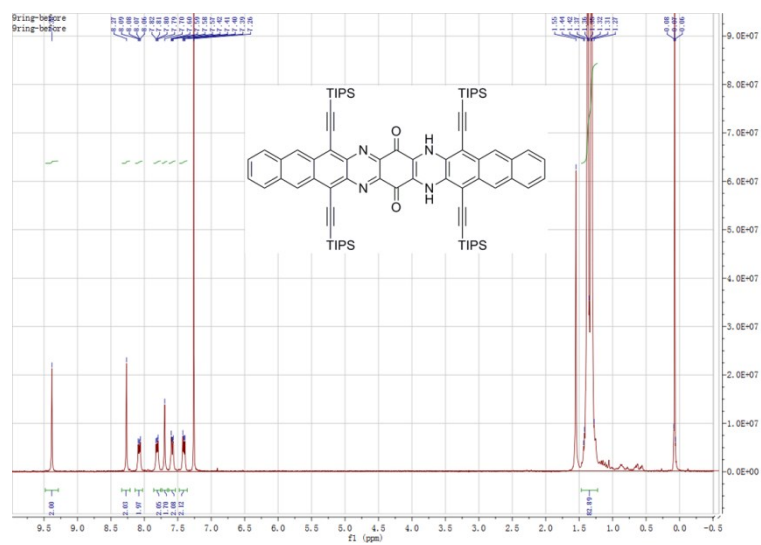


Figure S26. The ^1H NMR of compound HTAND.

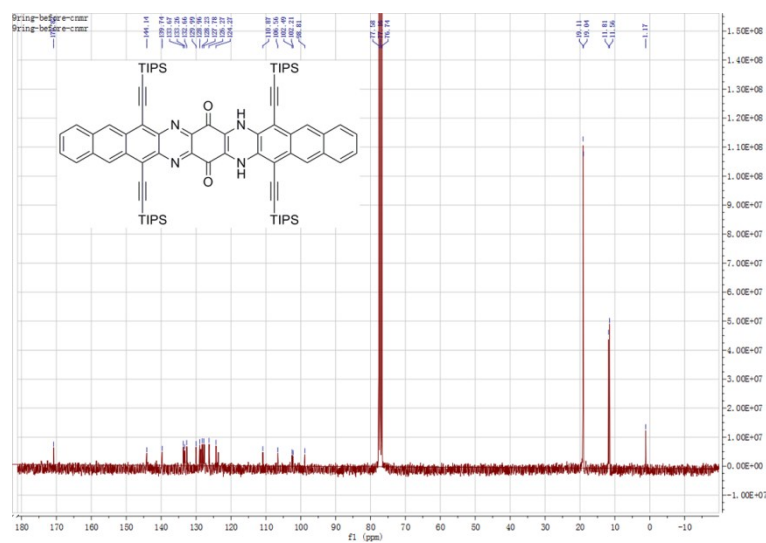


Figure S27. The ^{13}C NMR of compound HTAND.

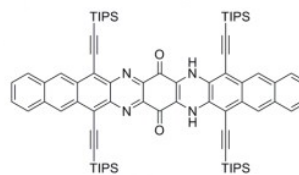
Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
 50 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
 Elements Used:
 C: 0-78 H: 0-99 N: 0-4 O: 0-2 Si: 0-4
 C78H98N4O2Si4
 LJB-5 449 (9.908) Cm (434-449)



1: TOF MS ES+
 1.01e+000

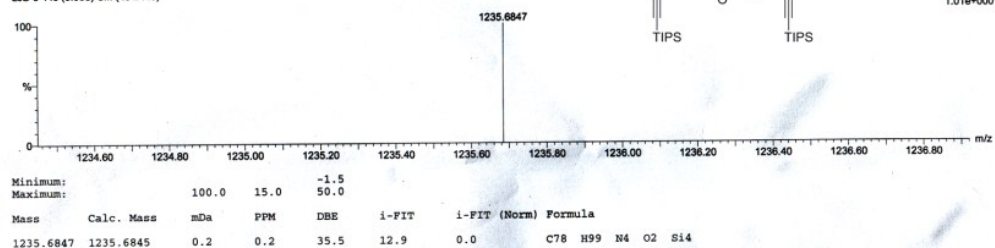


Figure S28. The HRMS of compound HTAND.

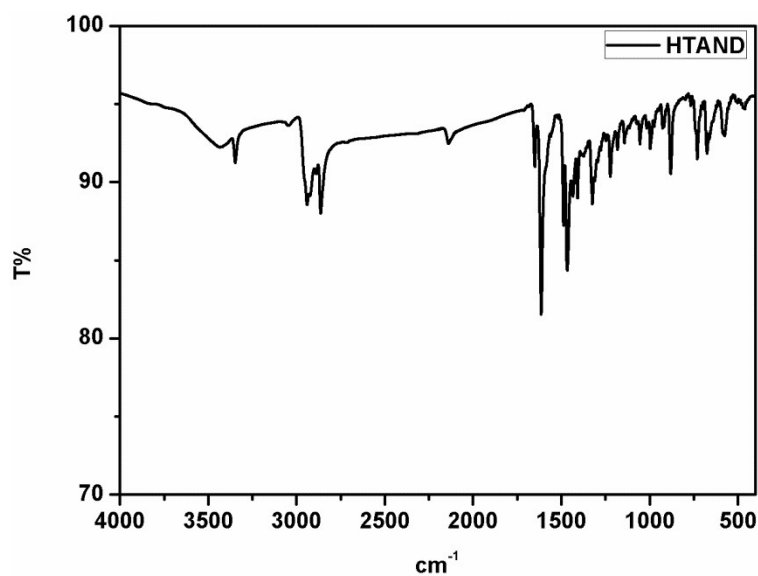


Figure S29. The FTIR of compound HTAND.

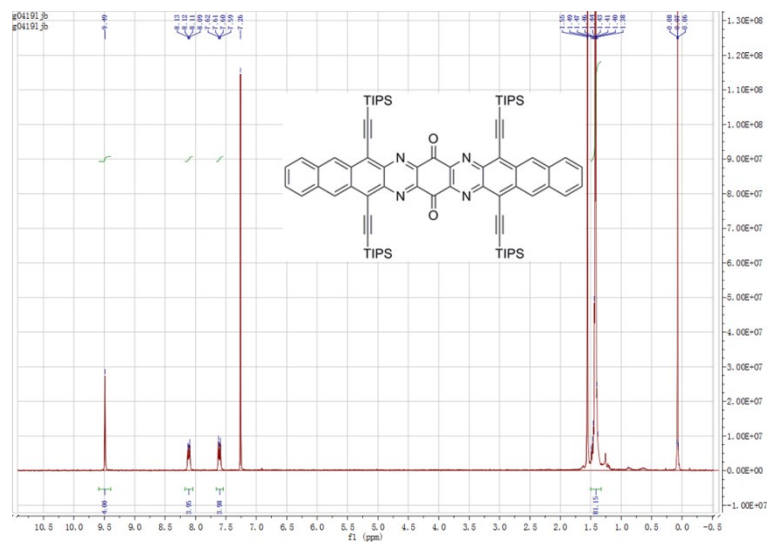


Figure S30. The ^1H NMR of compound TAND.

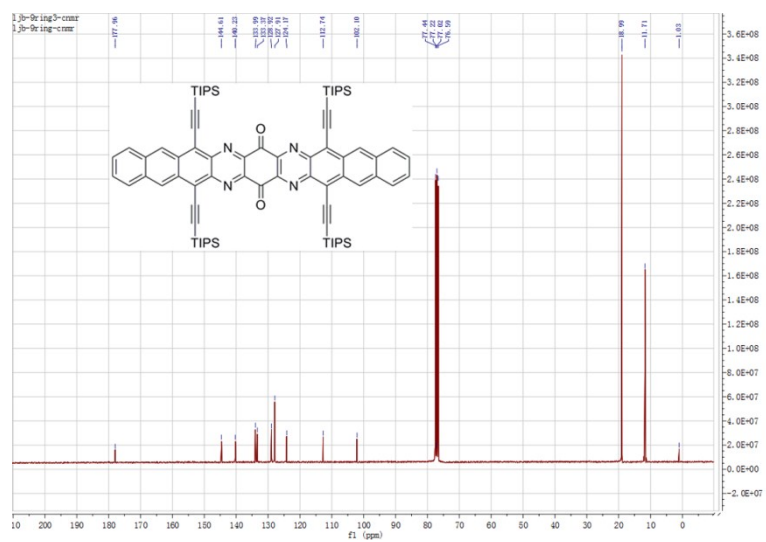


Figure S31. The ^{13}C NMR of compound TAND.

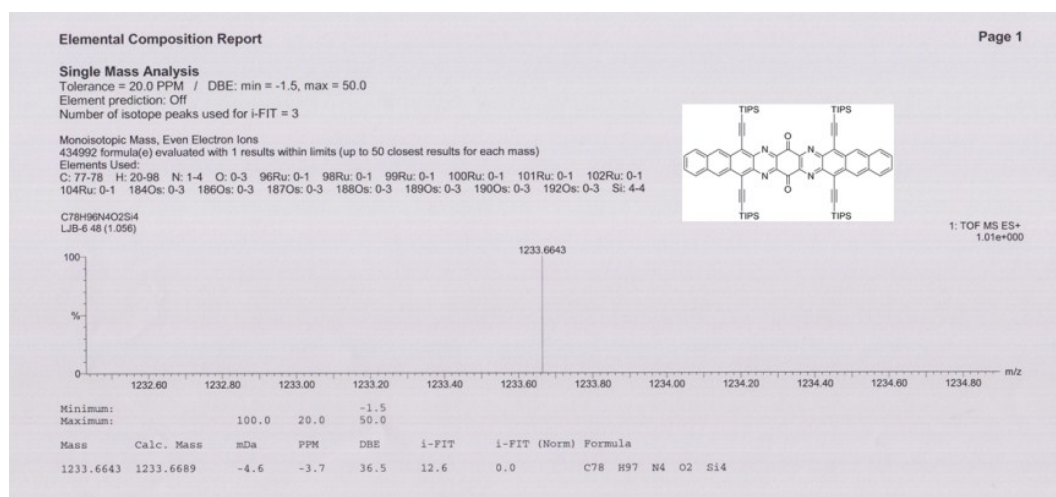


Figure S32. The HRMS of compound TAND.

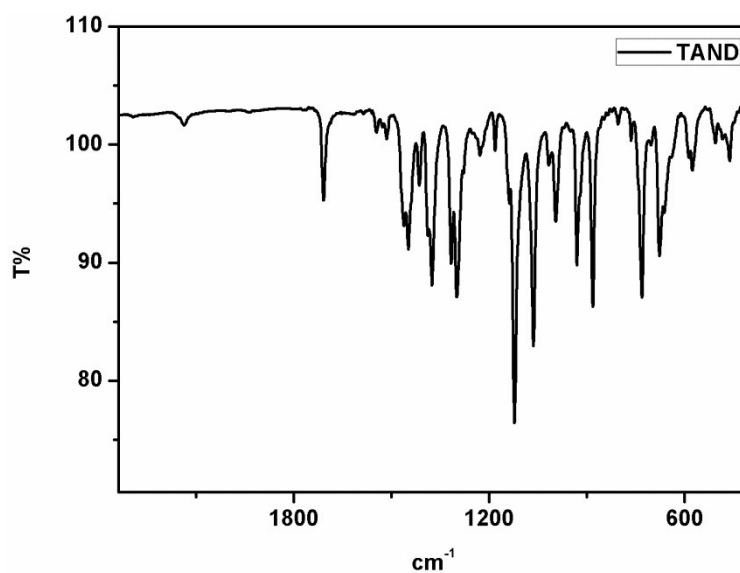


Figure S33. The FTIR of compound TAND.