Supplementary information

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

Junbo Li[a,b], Jianwei Miao[c], Guankui Long[a], Jing Zhang[a],Yongxin Li,[d] Ganguly Rakesh[d] Yang Zhao[a], Yi Liu,[e] Bin Liu[c]*, Qichun Zhang[a,d]*

[a]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

[b]School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430074, China

[c]School of chemistry and biomedical Engineering, Nanyang Technological Universtiy, Singapore 637459, Singapore

[d]Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

[e]The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, United States

Contents

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	C82 H102 N6 O2 Si4
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>2sigma(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 $e.Å^{-3}$

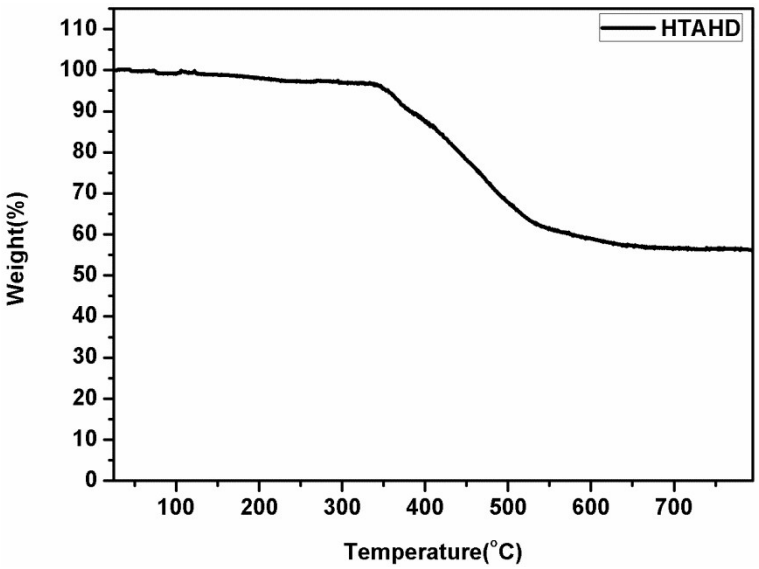

Figure S1. The TGA curve of H**TAHD**.

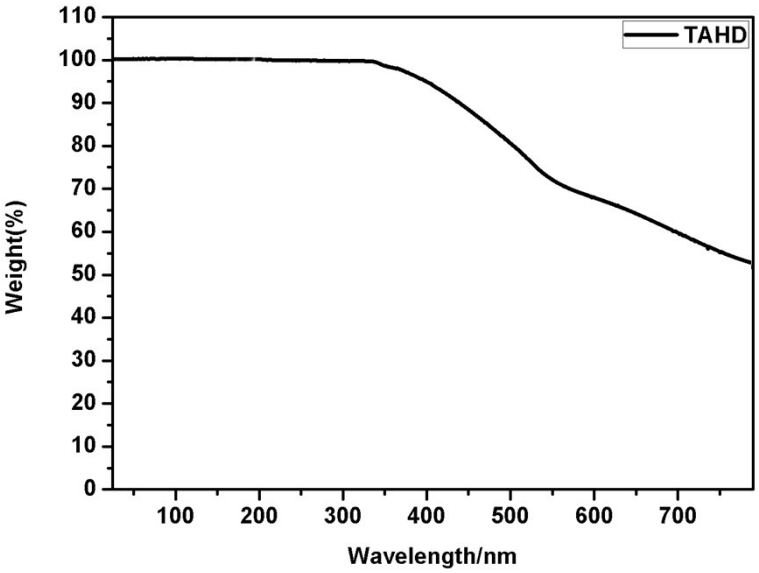

Figure S2. The TGA curve of **TAHD**.

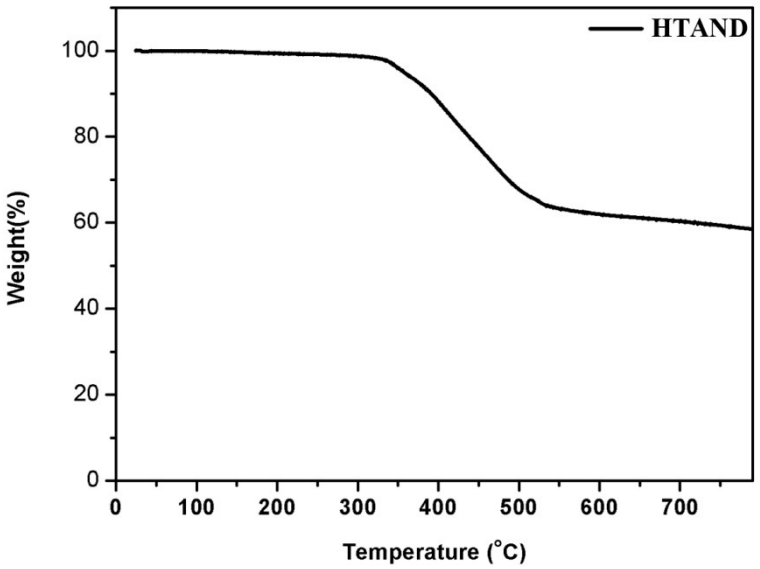

Figure S3. The TGA curve of **HTAND**.

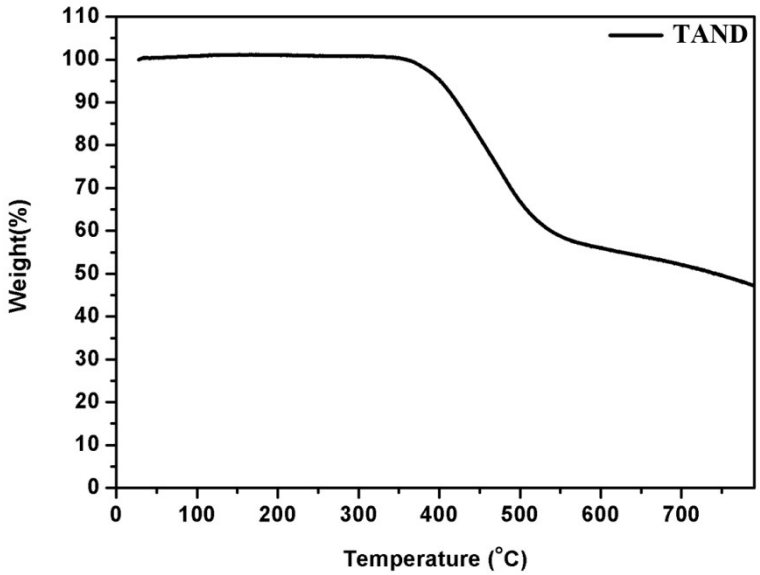

Figure S4. The TGA curve of **TAND**.

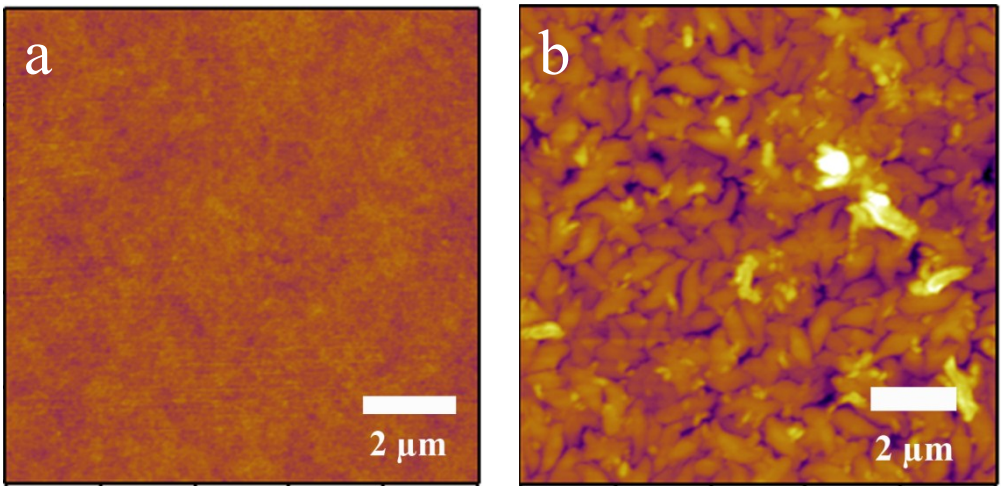

Figure S5. AFM images of (a) TAHD and (b) TAND thin films by spin-coating

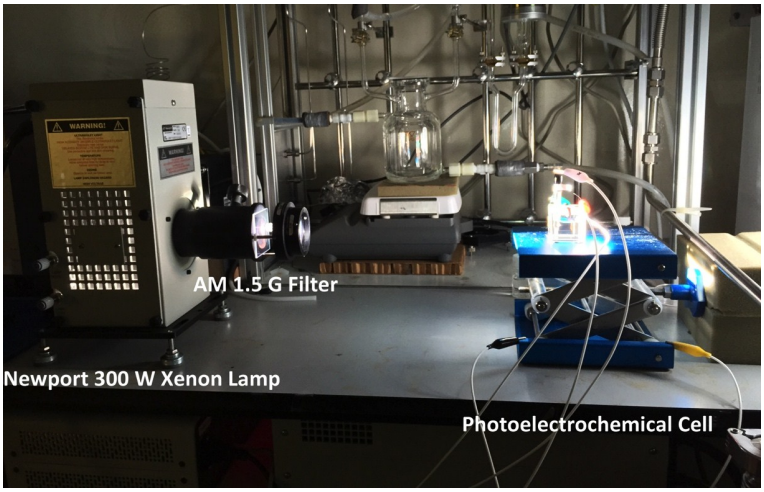

Figure S6. Experimental set-up for photoelectrochemical tests.

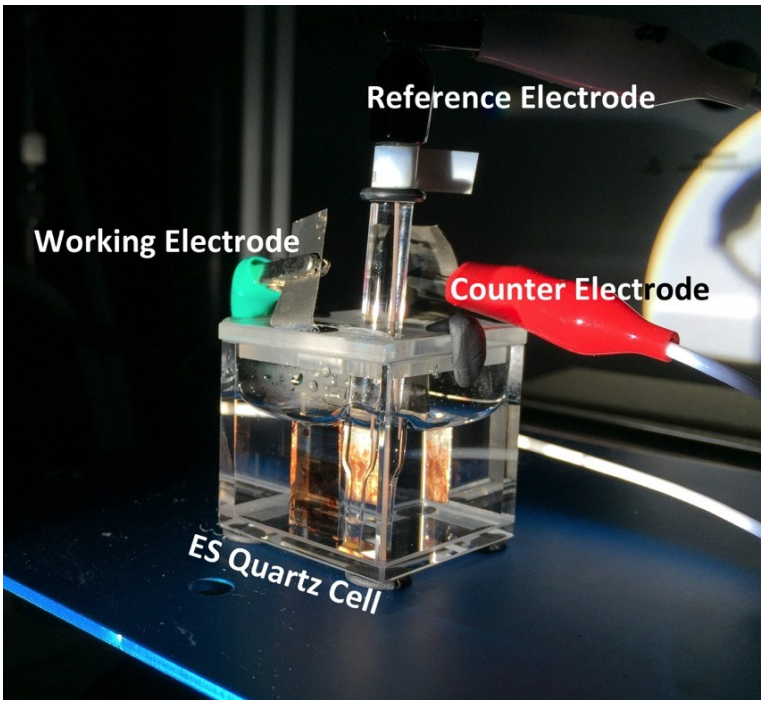

Figure S7. Photoelectrochemical cell (three electrode set-up) applied in this work.

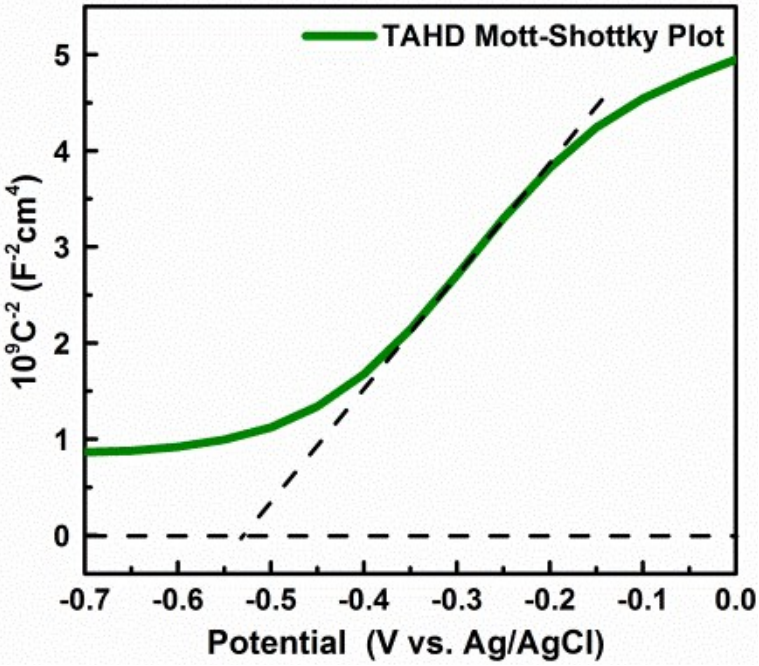

Figure S8. Mott-Schottky plot of **TAHD** measured at a frequency of 1000 Hz. The flat-band potential of **TAHD** is indicated by the intercept of the dashed lines.

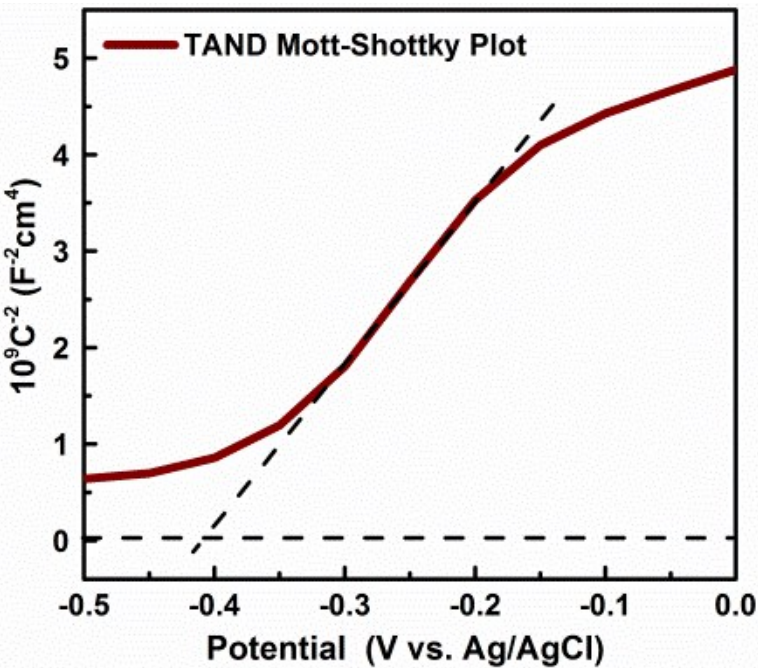

Figure S9. Mott-Schottky plot of **TAND** measured at a frequency of 1000 Hz. The flat-band potential of **TAND** is indicated by the intercept of the dashed lines.

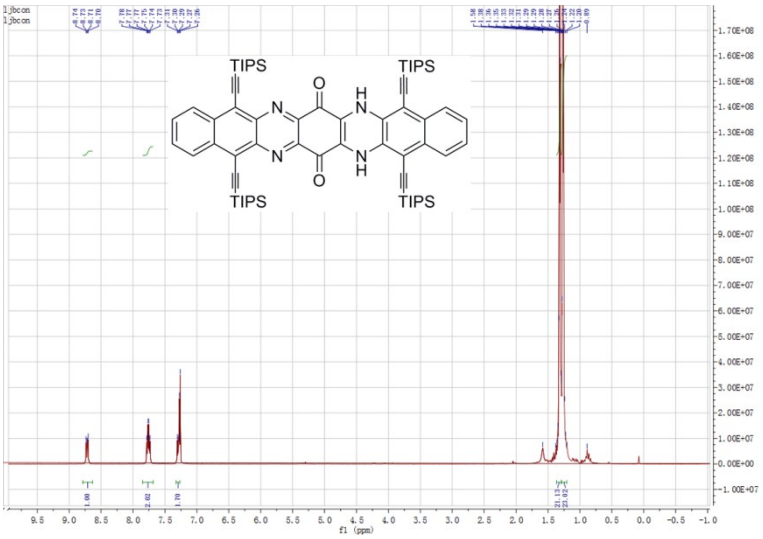

Figure S10. The ^{1}H NMR of compound **HTAHD**.

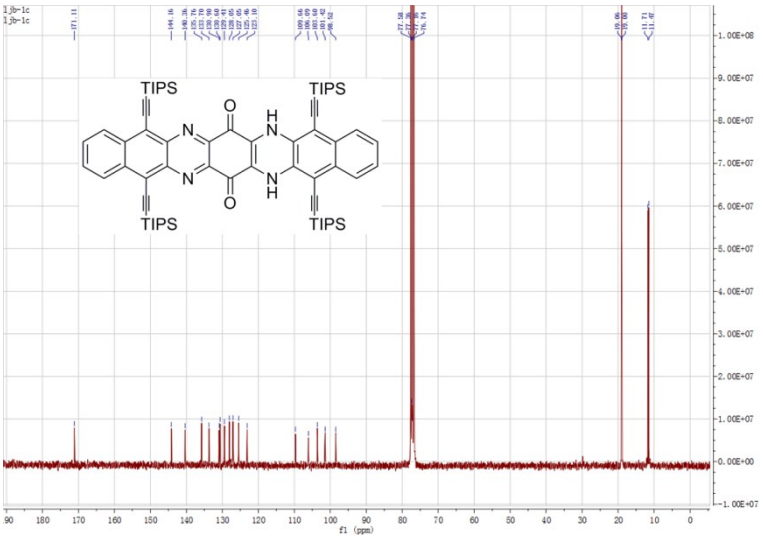

Figure S11. The ^{13}C NMR of compound **HTAHD**.

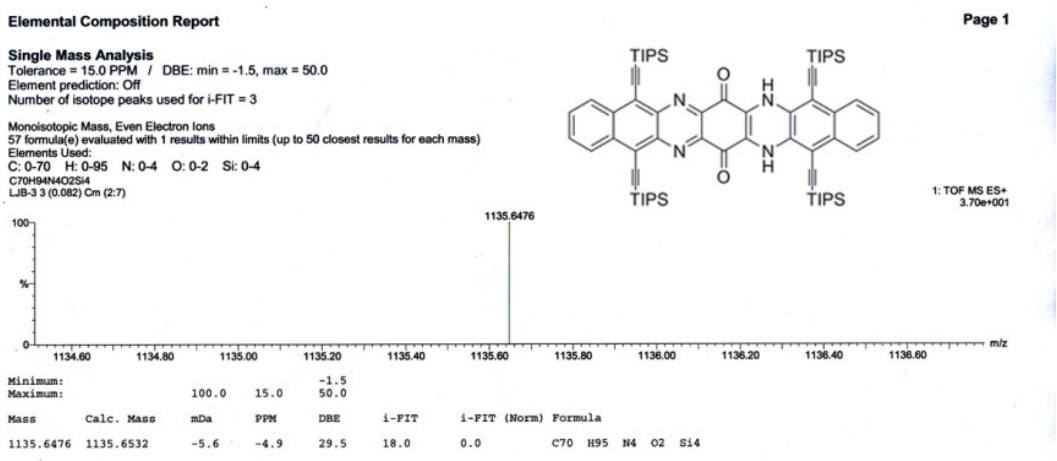

Figure S12. The HRMS of compound **HTAHD**.

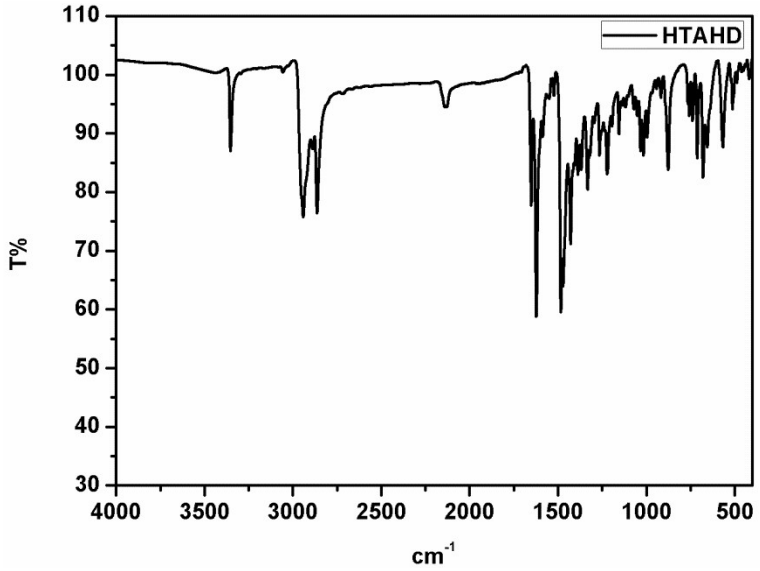

Figure S13. The FTIR of compound **HTAHD**.

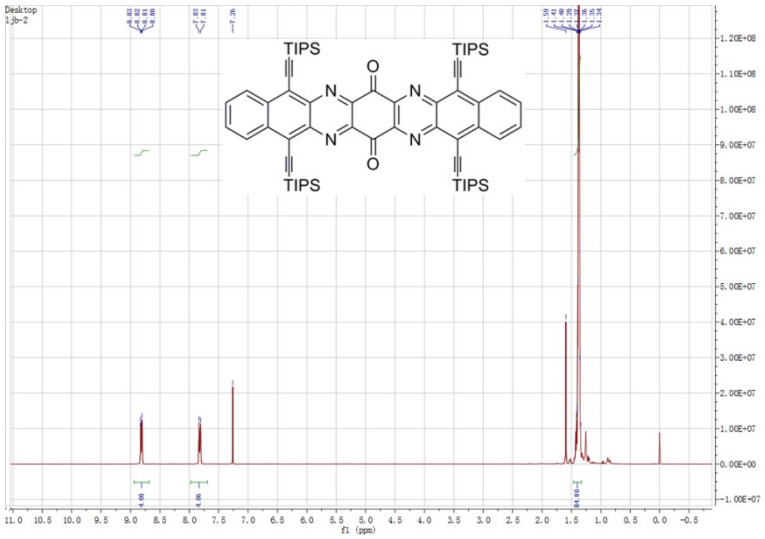

Figure S14. The ^{1}H NMR of compound **TAHD**.

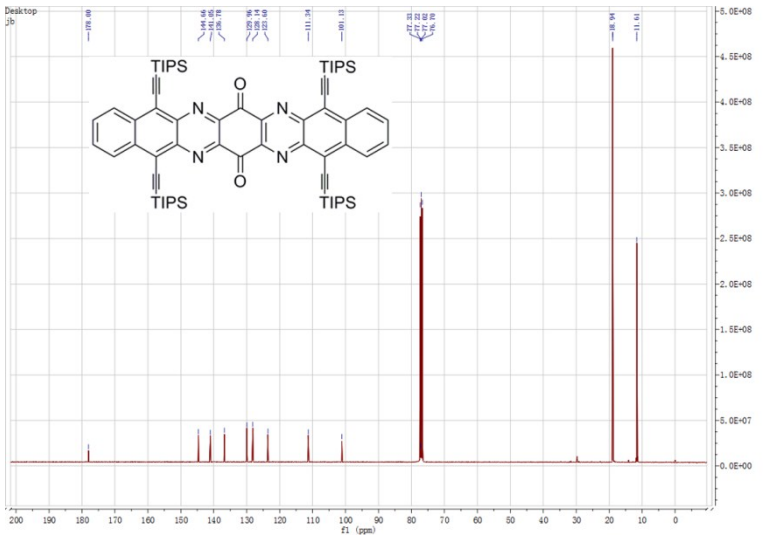

Figure S15. The ^{13}C NMR of compound **TAHD**.

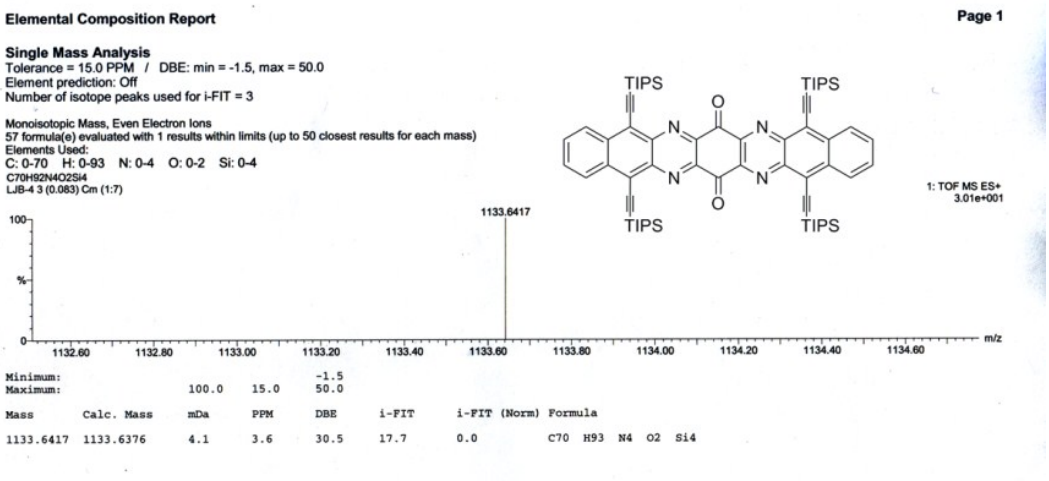

Figure S16. The HRMS of compound **TAHD**.

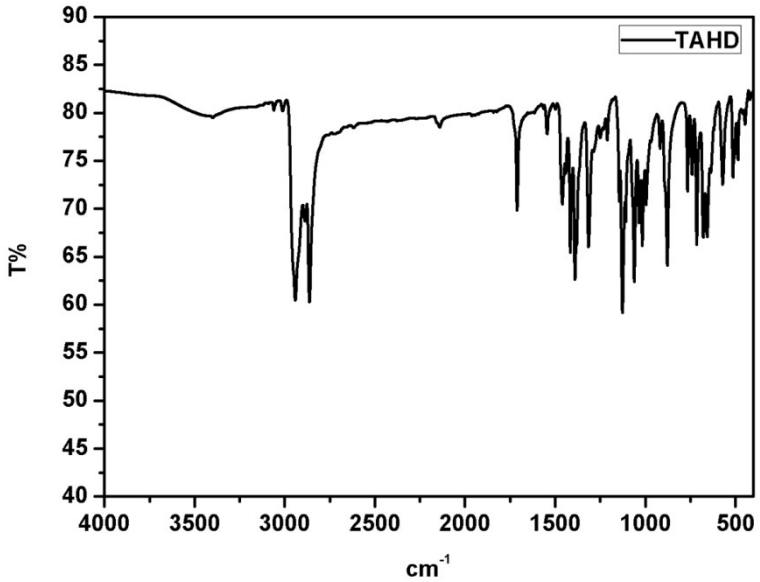

Figure S17. The FTIR of compound **TAHD**.

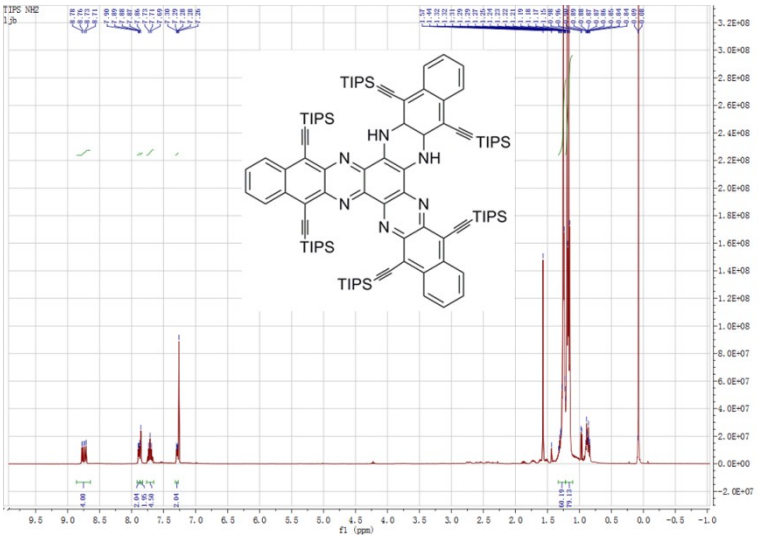

Figure S18. The ^{1}H NMR of compound **HHATA**.

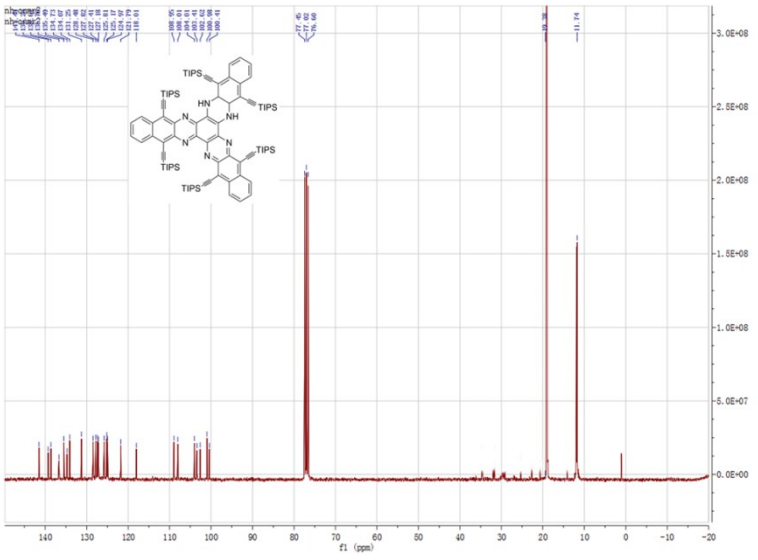

Figure S19. The ^{13}C NMR of compound **HHATA**.

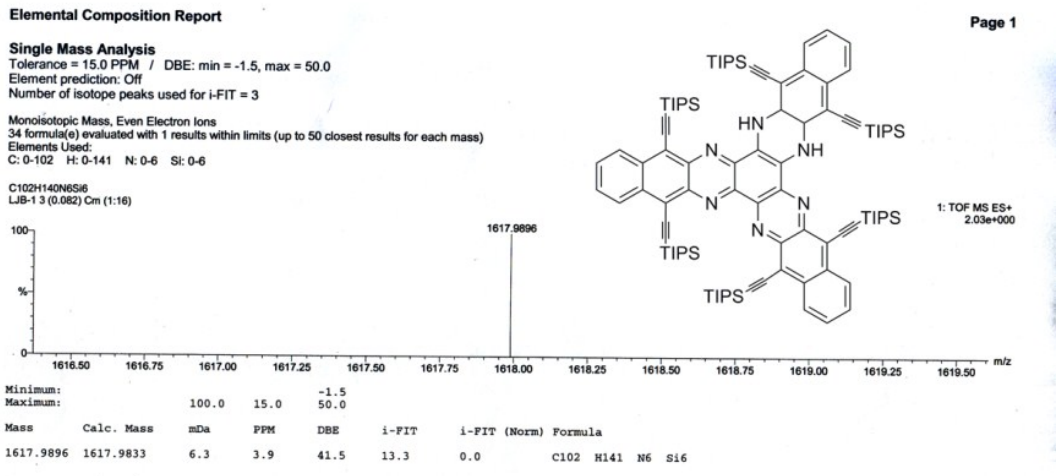

Figure S20. The HRMS of compound **HHATA**.

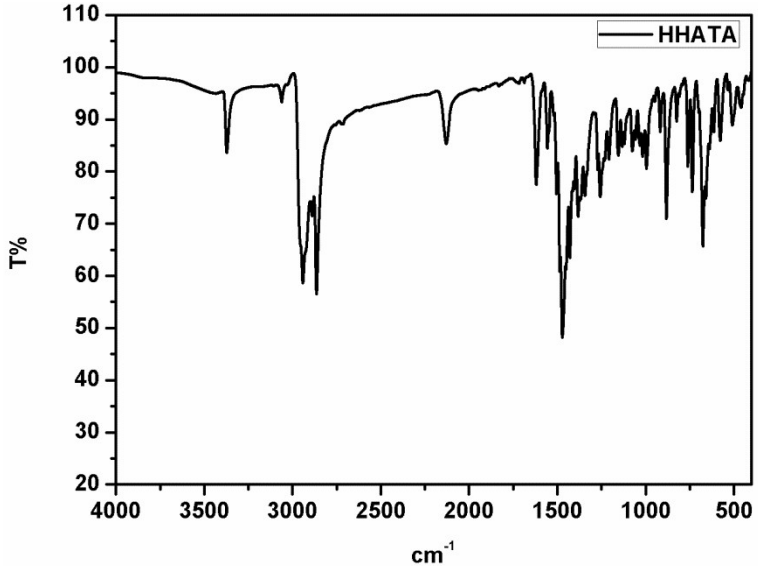

Figure S21. The FTIR of compound **HHATA**.

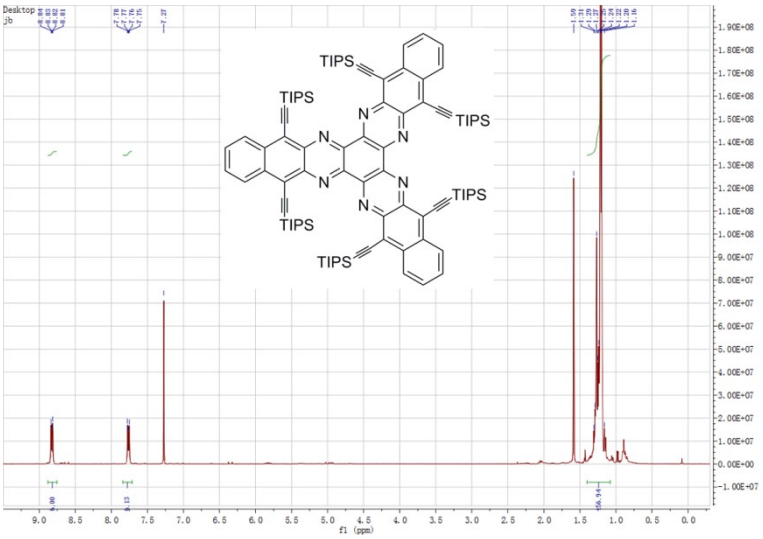

Figure S22. The ^{1}H NMR of compound **HATA**.

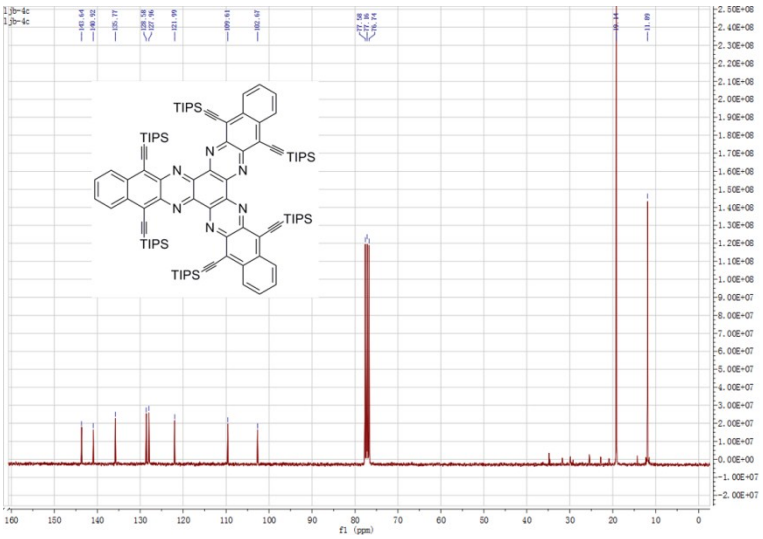

Figure S23. The ^{13}C NMR of compound **HATA**.

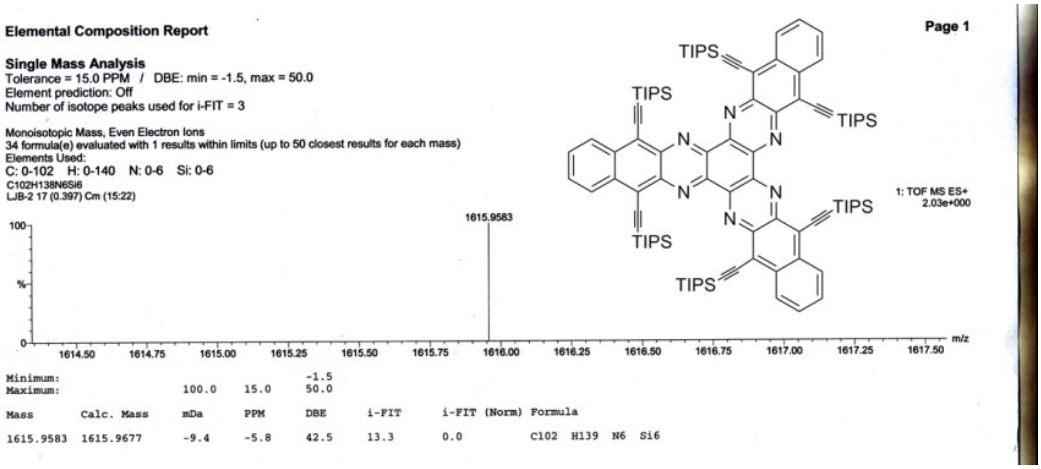

Figure S24. The HRMS of compound **HATA**.

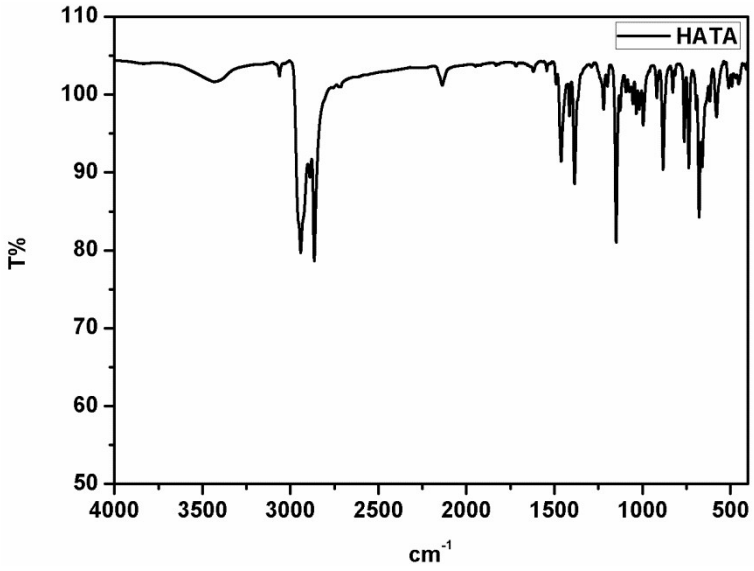

Figure S25. The FTIR of compound **HATA**.

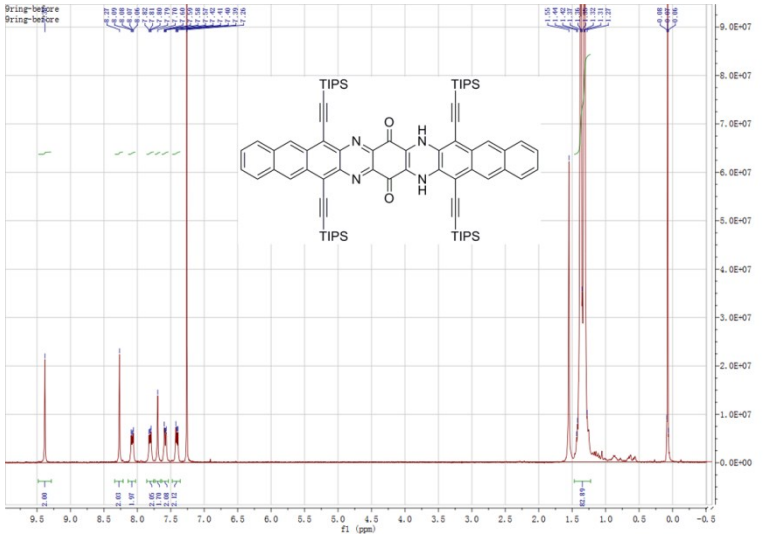

Figure S26. The ^{1}H NMR of compound **HTAND**.

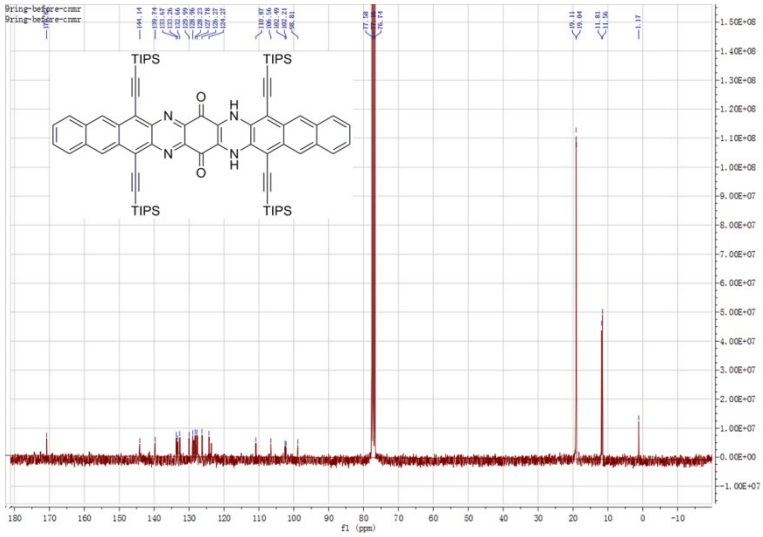

Figure S27. The ^{13}C NMR of compound **HTAND**.

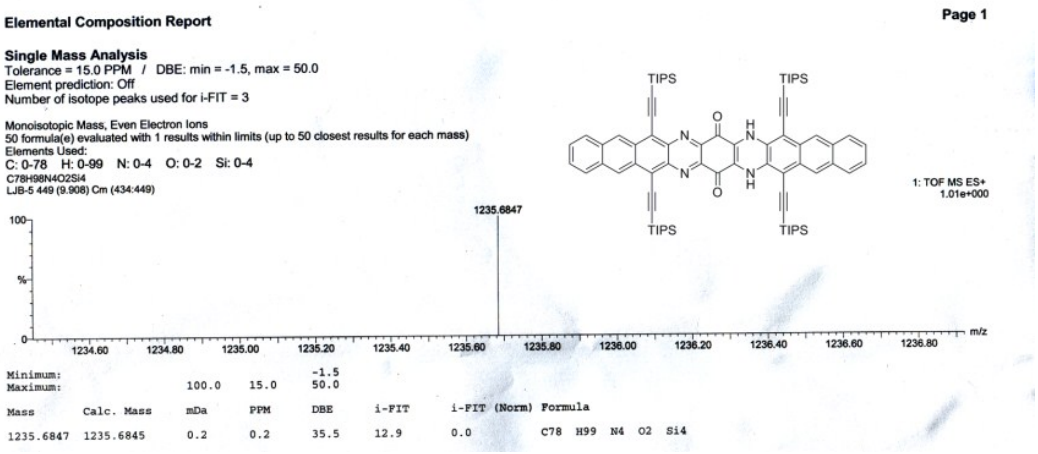

Figure S28. The HRMS of compound **HTAND**.

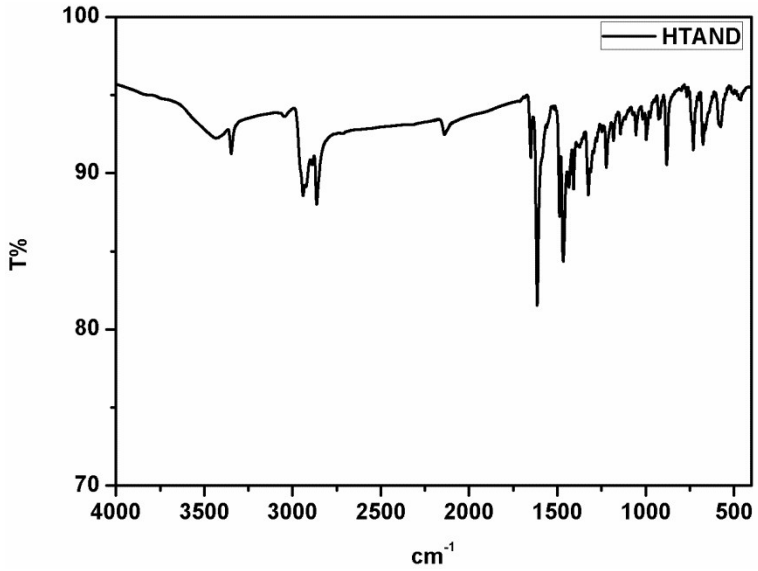

Figure S29. The FTIR of compound **HTAND**.

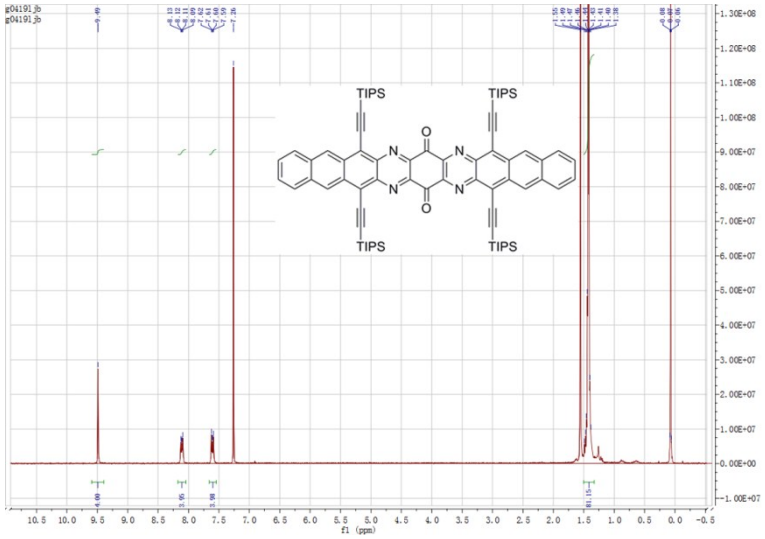

Figure S30. The ^{1}H NMR of compound **TAND**.

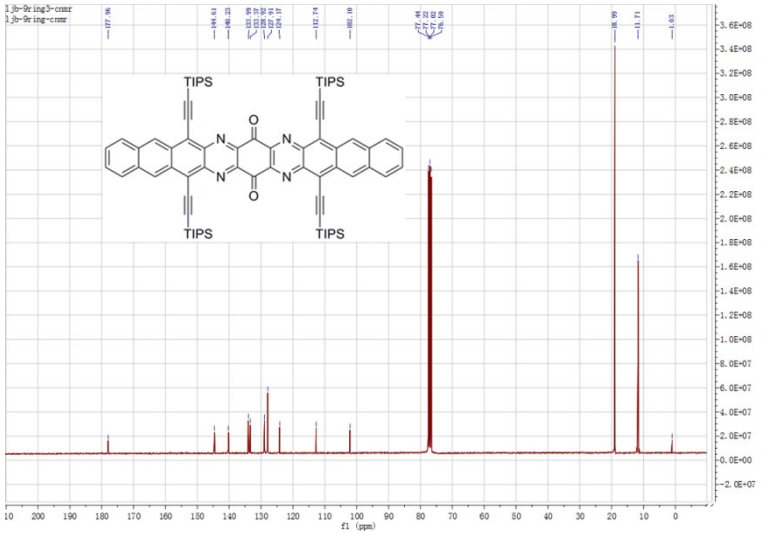

Figure S31. The ^{13}C NMR of compound **TAND**.

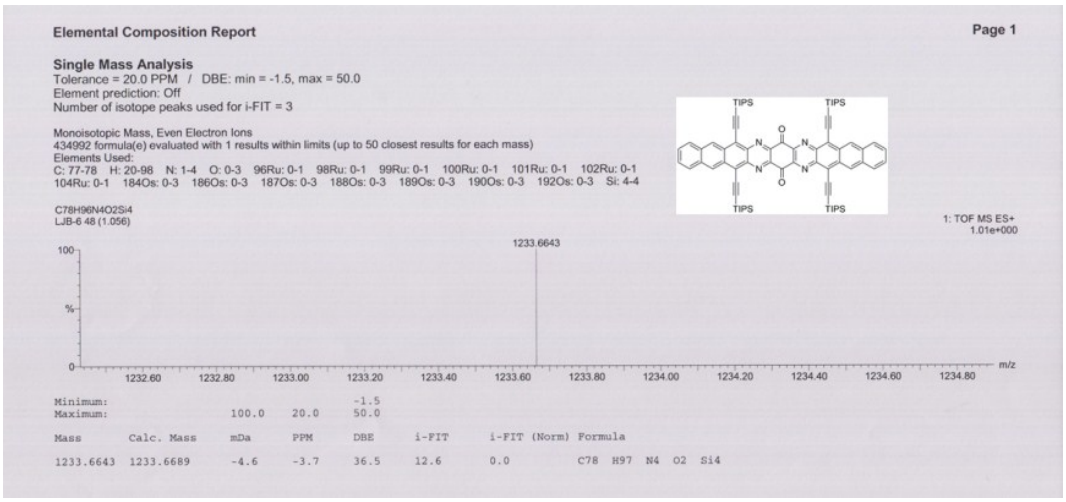

Figure S32. The HRMS of compound **TAND**.

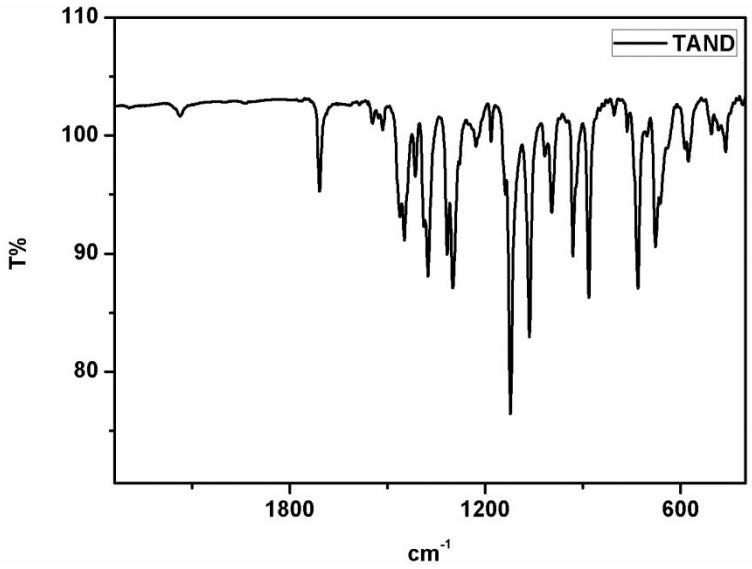

Figure S33. The FTIR of compound **TAND**.