Electronic Supplementary Material (ESI) for ChemComm.

# Supporting Information

## A Large Pyrene-Fused N-Heteroacene: Fifteen Aromatic Six-Member Rings Annulated in One Row

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## 1. Experiment method and instruments:

### Materials:

All the chemicals and solvents are purchased and used without further treatment if no special note. Tetrahydrofuran (THF) was dried by refluxing with Na and indicated by benzophenones. Dichloromethane (DCM) was dried by refluxing with $CaH_2$ for 24 h.

### Instruments and methods:

Electrospray ionization high-resolution mass spectrum (HR-MS (ESI)) was recorded on a Waters Q-Tof premierTM mass spectrometer. 1H-NMR and 13C-NMR were tested on Bruker Advance 300 spectrometer and the chemical shift values were given in ppm. UV-vis absorbance was tested on a Shimadzu UV-2501 spectrophotometer. Cyclic voltammetry was tested on a CHI 604E Electrochemical Analyzer. Glassy carbon (diameter: 1.6 mm; area 0.02 cm2) was used as working electrode, platinum wires were used as counter electrode and reference electrode, respectively. $^nBu_4NPF_6$ (0.1M) was used as supporting electrolyte. Potential was recorded in an anhydrous DCM solution and the scanning rate was 50 mV/s. Fc+ /Fc (HOMO = -4.80 eV) was used as an external standard.

### Femtosecond Transient Absorption Spectroscopy:

A Ti:sapphire femtosecond laser system provided laser pulses for the femtosecond transient absorption measurements. A regenerative amplifier (Spectra Physics, Spitifire) seeded with a mode-locked Ti:sapphire laser (Spectra Physics, Tsunami) delivered laser pulses at 800 nm (120 fs, 1 kHz), which were then divided into two components by using a 9:1 beam splitter. The major component was sent to an optical parametric amplifier (Spectra Physics, OPA-800CF) to generate the pump pulses (480 nm, 130 fs, 1 kHz). The minor component was further attenuated and focused into a 3-mm sapphire plate to generate the probe pulses. A band-pass filter (SPF-750, CVI) was inserted into the probe beam to select visible probe (420–750 nm). The time delay between the pump and probe beams were regulated through a computer-controlled motorized translation stage in the pump beam. A magic scheme was adopted in the pump-probe measurement when necessary. The temporal resolution between the pump and the probe pulses was determined to be ~150 fs (FWHM). The transmitted light was detected by a CMOS linear image sensor (S8377-512Q, Hamamatsu). The excitation pulsed energy was ~ 50 nJ/pulse as measured at the sample site. The stability of the samples was spectrophotometrically checked before and after each experiment. Analysis of the kinetic traces derived from time-resolved spectra was performed using nonlinear least-square fitting to a general sum-of-exponentials function after deconvolution of instrument response function (IRF).

**Single-crystal X-ray diffraction:**

The suitable single-crystal (0.02 × 0.06 × 0.08 mm) was selected for single-crystal X-ray data collection with a Bruker SMART APEX-II CCD area detector on a D8 goniometer. The data were collected using graphite-monochromated and Cu Kα radiation ($\lambda$ = 1.54178 Å) with the ω scan method at 153 K. The data were processed with the SAINT program of the APEX3 software for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SADABS program for area detector. All structures were solved by the direct method and refined by the full-matrix least-squares method on F2 (SHELX-97).[1] All non-H atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included as riding with Uiso (H) = 1.2 Ueq (C). Crystallographic data and structural refinements are summarized in Table S1.

CCDC 1537461 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## 2. Crystallographic data and structural refinements

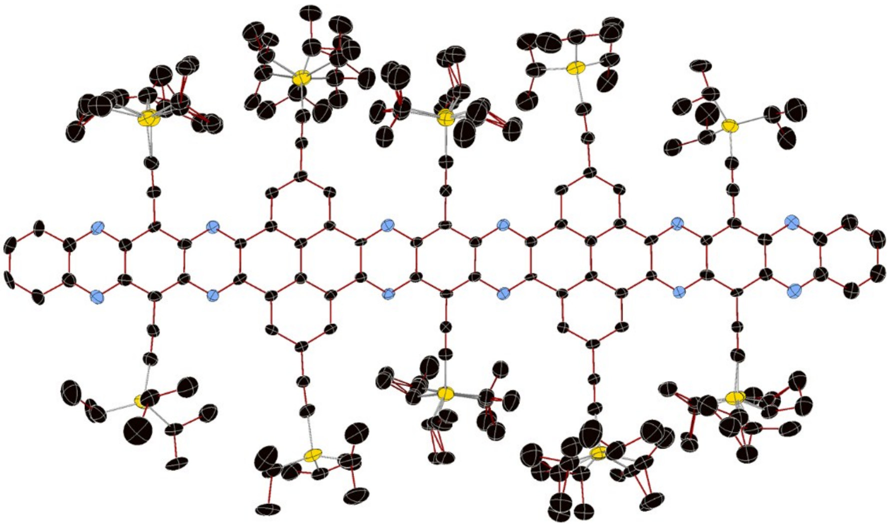


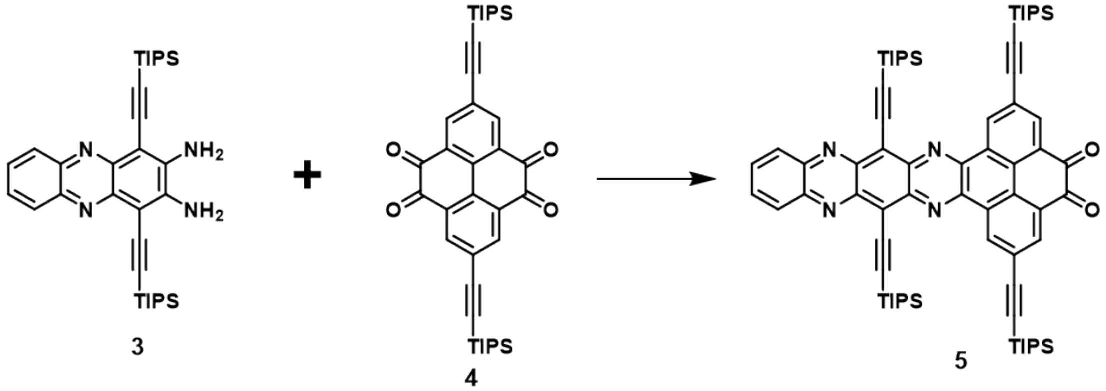
Figure S1. The ellipsoid plot of the **15RINGS** shows that the atomic thermal ellipsoids of carbon and nitrogen atoms in the skeleton are acceptable although the TIPS chains are disorder in some degree. (50% probability ellipsoid, color sheme: C, black; N, blue; Si, yellow. H atoms are omitted for clarity).

**Table S1**: Crystallographic data and structure refinement parameters of the compound **15RINGS**.

| | **15RINGS** |
|---|---|
| $T$ (K) | 153 (2) |
| Formula | $C_{364}$ $H_{450}$ $N_{24}$ $O_{10}$ $Si_{20}$ |
| Formula weight | 5883.25 |
| Crystal system | triclinic |
| Space group | $P$ |
| Z | 1 |
| $a$ (Å) | 20.1652 (5) |
| $b$ (Å) | 21.0142 (5) |
| $c$ (Å) | 21.8327 (6) |
| $\alpha$ (deg) | 70.114 (2) |
| $\beta$ (deg) | 89.128 (2) |
| $\gamma$ (deg) | 89.198 (2) |
| $V$ (Å$^3$) | 8698.7 (4) |
| $\rho$ calcd (g/cm$^3$) | 1.123 |
| λ (Cu Kα) (Å) | 1.54178 |
| Collected reflns | 63252 |
| Unique reflns | 29982 |
| Parameters | 2447 |
| $R$ (int) | 0.2658 |
| $R_1$ [$I > 2\sigma(I)$] | 0.1019 |
| $wR_2$ [$I > 2\sigma(I)$] | 0.2314 |
| GOF | 0.931 |

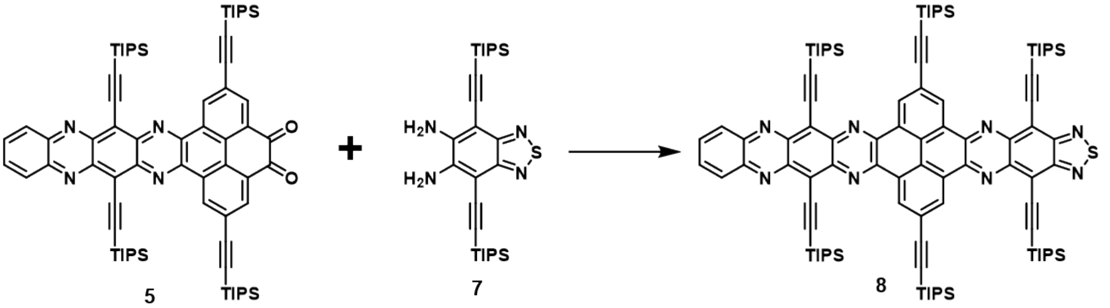
## 3. Synthesis details:

**2,7,10,17-tetra((triisopropylsilyl)ethynyl)phenanthro[4,5-abc]quinoxalino[2,3-i]phenazine-4,5-dione (5).**



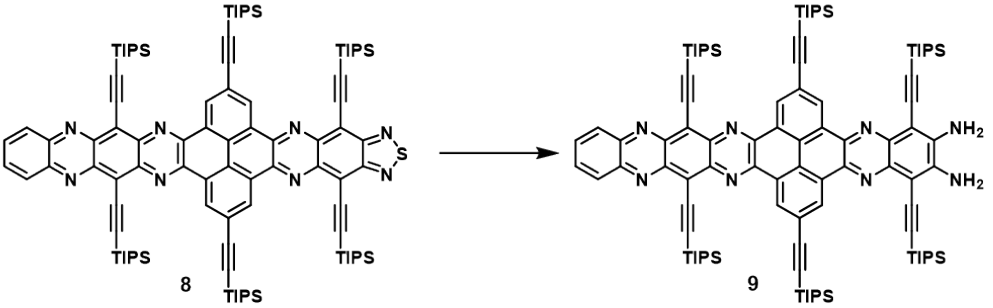
1,4-bis((triisopropylsilyl)ethynyl)phenazine-2,3-diamine **3** (623 mg, 1mmol) and 2,7-bis((triisopropylsilyl)ethynyl)pyrene-4,5,9,10-tetraone **4** (114 mg, 0.2 mmol) were dissolved in a mix solvent of $CHCl_3$ (100 mL) and AcOH (50 mL). Then the orange solution was refluxed under argon at 80 ℃ for 36 h. After that, the solvent was removed by rotary evaporation, and the residue solid was purified by silica column chromatography ($CH_2Cl_2$: hexane = 1:3). The excess compound **4** was collected to be reused. The crude product **5** (blackish green in solution) and its reduced form compound (red color in solution, almost the same $R_f$ on TLC with compound **5**) were collected together, and then dried under reduced pressure at 60 ℃and treated with excess amount active $MnO_2$ (1g) in dry methylene chloride (20 mL) at room temperature for 2 h. Then $MnO_2$ was removed by filtrated through celite and washed with methylene chloride until the filtrate was colorless. After removing the solvent, the solid was dissolved in small amount $CHCl_3$ and reprecipitated by adding methanol (50 mL). The solid was collected by filtration and washed with methanol (20 mL X 2) to afford pure compound **5** (160 mg, 0.14 mmol, 70%) as black solid. $^1$H NMR (300 MHz, CDCl3): δ = 9.63 (s, 2H), 8.58 (s, 2H), 8.28 (m, 2H), 7.91 (m, 2H), 1.43 (br, 42H) 1.25 (br, 42H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.65, 145.41, 143.40, 142.74, 141.62, 137.81, 135.62, 132.29, 131.06, 130.48, 130.29, 130.12, 125.85, 123.04, 112.63, 104.67, 102.40, 96.67, 19.11, 18.78, 11.67, 11.48. HR-MS (ESI) m/z Calc. for $[M+H]^+$ $C_{72}H_{93}N_4O_2Si_4$: 1157.6376, found : 1157.6349.

**Compound 8**



Compound **5** (231 mg, 0.2 mmol) and Compound **7** (116 mg, 0.22 mmol) were dissolved in a mix solvent of $CHCl_3$ (30 mL) and AcOH (15 mL) and refluxed under argon at 80 ℃ for 30 h. Then the solvent was removed by rotary evaporation, and the residue was purified by silica column chromatography ($CH_2Cl_2$: hexane = 1:3). The crude product **8** was dissolved in small amount $CHCl_3$ and reprecipitated by adding methanol (60 mL). The solid was collected by filtration and washed with methanol (20 mL X 2) to afford pure compound **8** (180 mg, 0.12 mmol, 60%) as black solid. H NMR (300 MHz, CDCl3): δ = 9.82 (s, 2H), 9.74 (s, 2H), 8.32 (m, 2H), 7.92 (m, 2H), 1.49 – 1.22 (m, 126H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 155.29, 145.22, 144.18, 144.17, 143.41, 141.84, 141.61, 133.39, 133.27, 131.97, 130.45, 130.23, 130.03, 128.40, 124.73, 122.72, 114.52, 112.14, 111.24, 105.90, 102.66, 101.71, 94.34, 19.15, 19.03, 18.88, 12.08, 11.69, 11.53. HR-MS (ESI) m/z Calc. for $[M+H]^+$ $C_{100}H_{135}N_8Si_6S$: 1647.9146, found : 1647.9116.

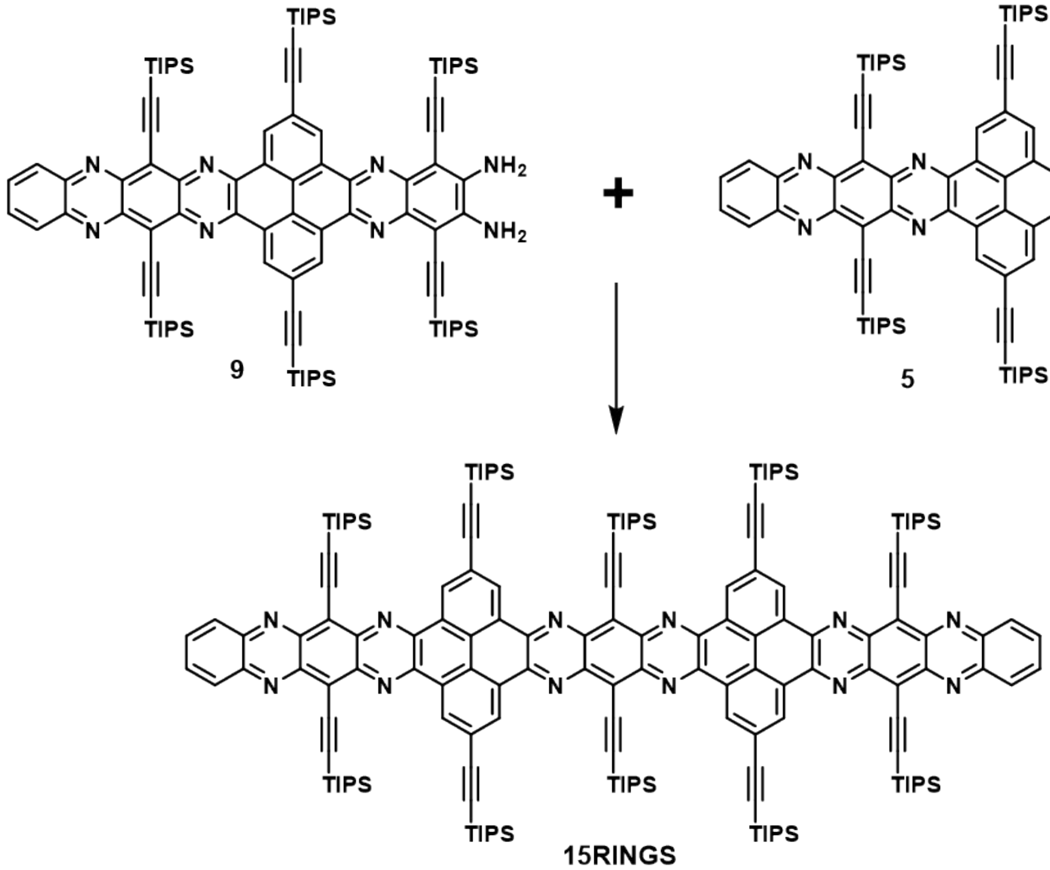
**Compound 9.**



Compound **8** (165 mg, 0.1 mmol) was dissolved in dry THF (15 mL) under argon and stirred at 0 ℃. Then $LiAlH_4$ (38 mg, 1mmol) was slowly added. After that, the reaction mixture was allowed to warm to room temperature and stirred for 14 h. The reaction was confirmed to complete by TLC and quenched with saturated, aqueous $NH_4Cl$ solution. The mixture was extracted with diethyl ether (30 mL X 3). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure to afford compound **9** as brownish black solid (155 mg, 95%). $^1H$

NMR (300 MHz, CDCl3): δ = 9.78 (s, 4H), 8.31 (m, 2H), 7.91 (m, 2H), 4.96 (br, 4H) 1.49-1.20 (m, 126H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 145.08, 145.01, 143.44, 143.35, 141.98, 139.65, 138.92, 131.87, 131.74, 131.17, 130.91, 130.44, 129.79, 127.14, 123.83, 122.47, 111.68, 106.68, 104.31, 103.47, 102.75, 100.98, 93.01, 19.15, 19.04, 18.89, 12.10, 11.69, 11.37. HR-MS (ESI) m/z Calc. for $[M+H]^+$ $C_{100}H_{139}N_8Si_6$: 1619.9738, found : 1619.9731.

**Compound 15RINGS.**



Compound **9** (32 mg, 0.02 mmol) and Compound **5** (23 mg, 0.02 mmol) were dissolved in a mixed solvent of $CHCl_3$ (20 mL) and AcOH (5 mL) and refluxed under argon at 80 ℃ for 48 h. Then the solvent was removed by rotary evaporation, and the residue was purified by silica column chromatography ($CH_2Cl_2$: hexane = 1:3). The crude product **15RINGS** was dissolved in small amount $CHCl_3$ and reprecipitated by adding methanol (30 mL). The solid was collected by filtration and washed with methanol (10 mL X 2) to afford pure compound **15RINGS** (25 mg, 0.009 mmol, 46%) as black solid. $^{1}$H NMR (300 MHz, CDCl3): δ = 9.89 (d, 8H), 8.33 (m, 4H), 7.93 (m, 4H), 1.60-1.22 (m, 240H (This number is larger than the theoretical number of 210, since the peak of $H_2O$ was merged in these peaks.)). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 145.26, 144.37, 144.03, 143.51, 142.62, 141.95, 133.51, 133.40, 132.02, 130.52, 130.32, 130.24, 128.48, 124.74, 122.77, 122.28, 112.12, 111.79, 106.06, 102.75, 102.46, 94.50, 19.29, 19.16, 18.92, 12.13, 11.71, 11.58. HR-MS (ESI) m/z Calc. for $[M+Na]^+$ $C_{172}H_{228}N_{12}Na^{28}Si_8{}^{29}Si_2$: 2766.5792, $C_{172}H_{228}N_{12}Na^{29}Si_9{}^{30}Si$: 2766.5769, found :

2766.5842.

## 4. $^1$H NMR, $^{13}$C NMR and HR-MS spectra of all the new compounds:

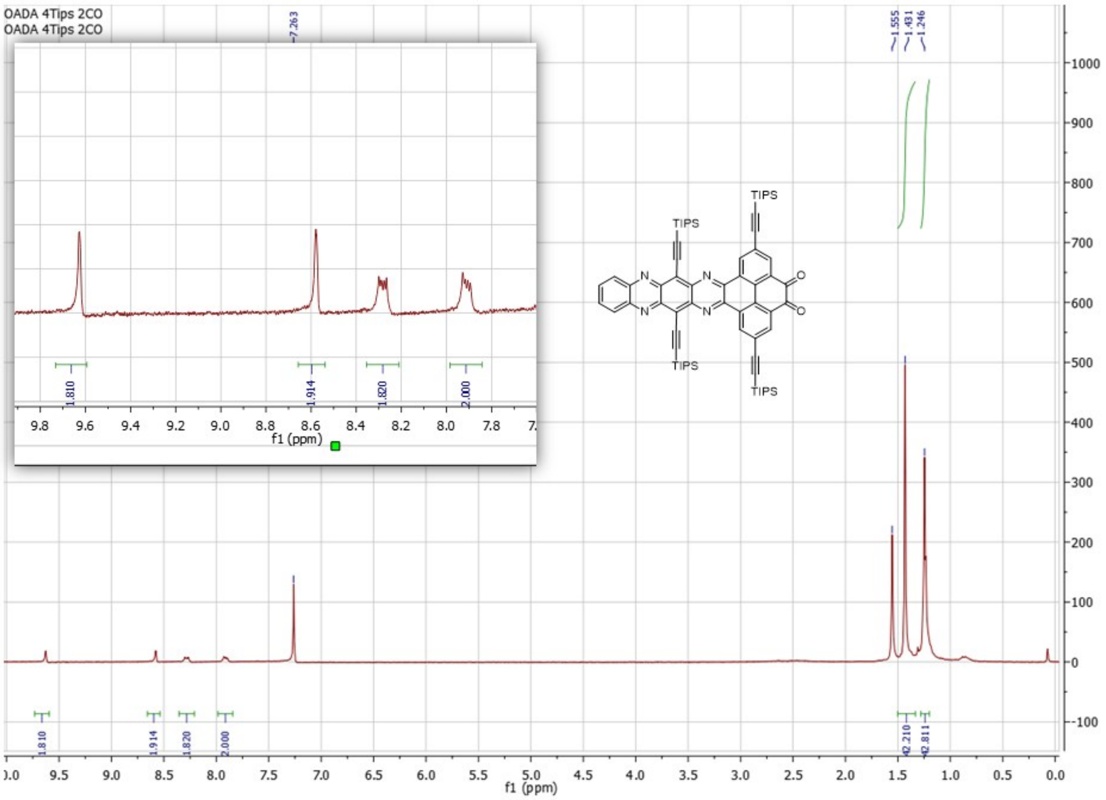


Figure S2. $^1$H NMR spectrum of compound **5**.

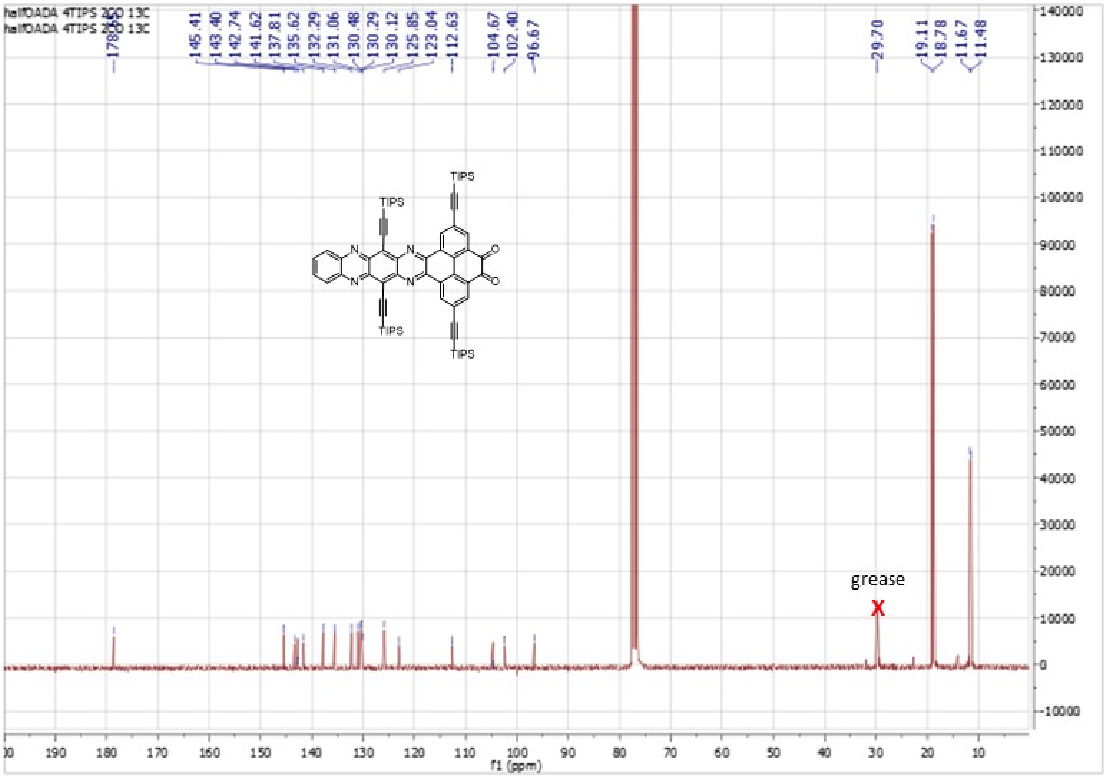


Figure S3. $^{13}$C NMR spectrum of compound **5**.

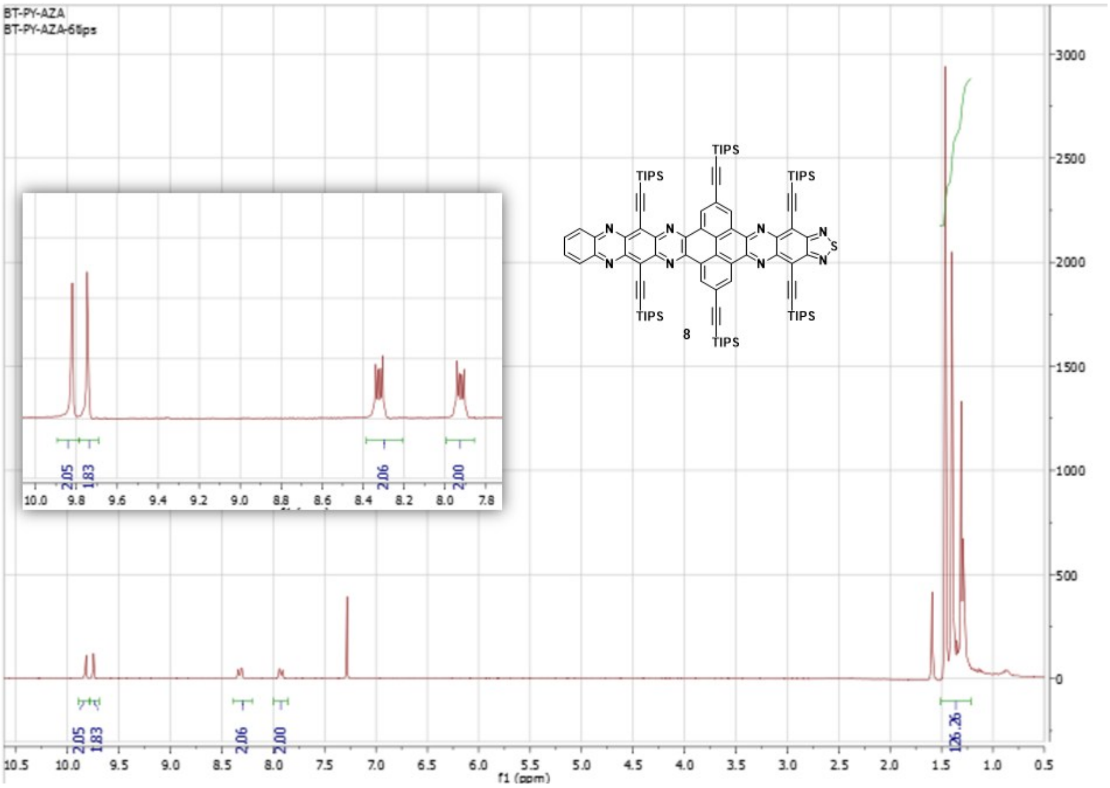


Figure S4. $^{1}$H NMR spectrum of compound **8**.

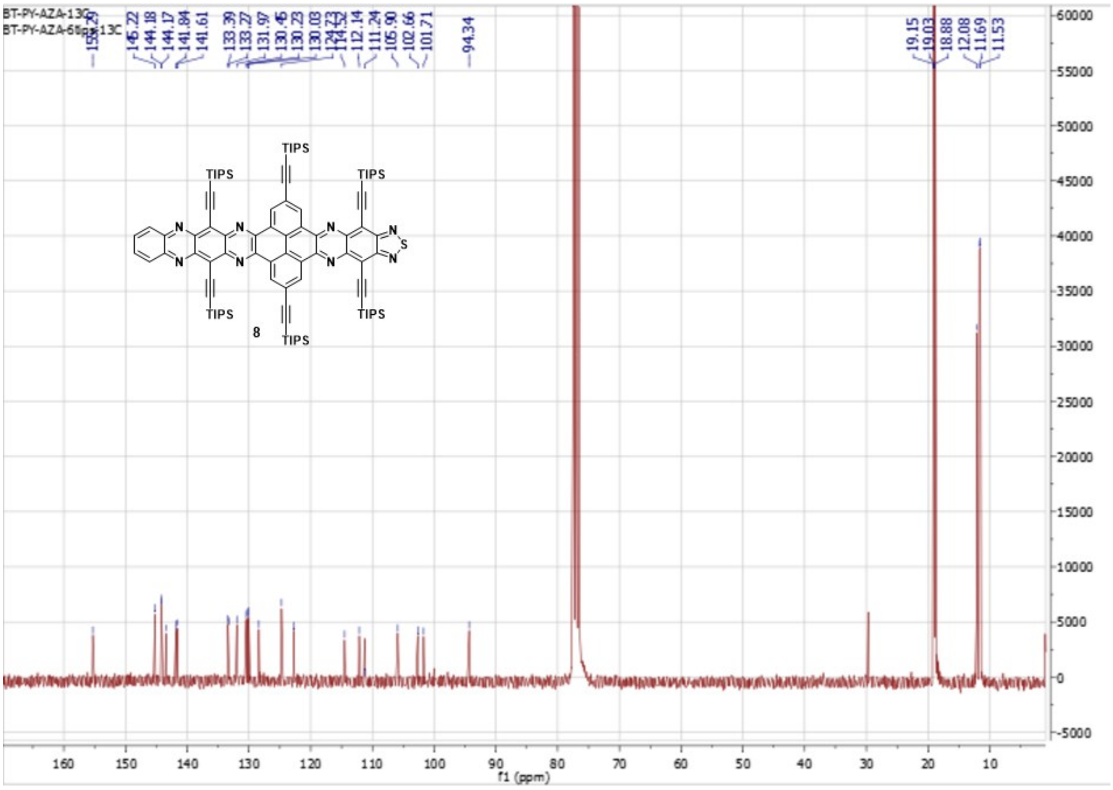


Figure S5. $^{13}$C NMR spectrum of compound **8**.

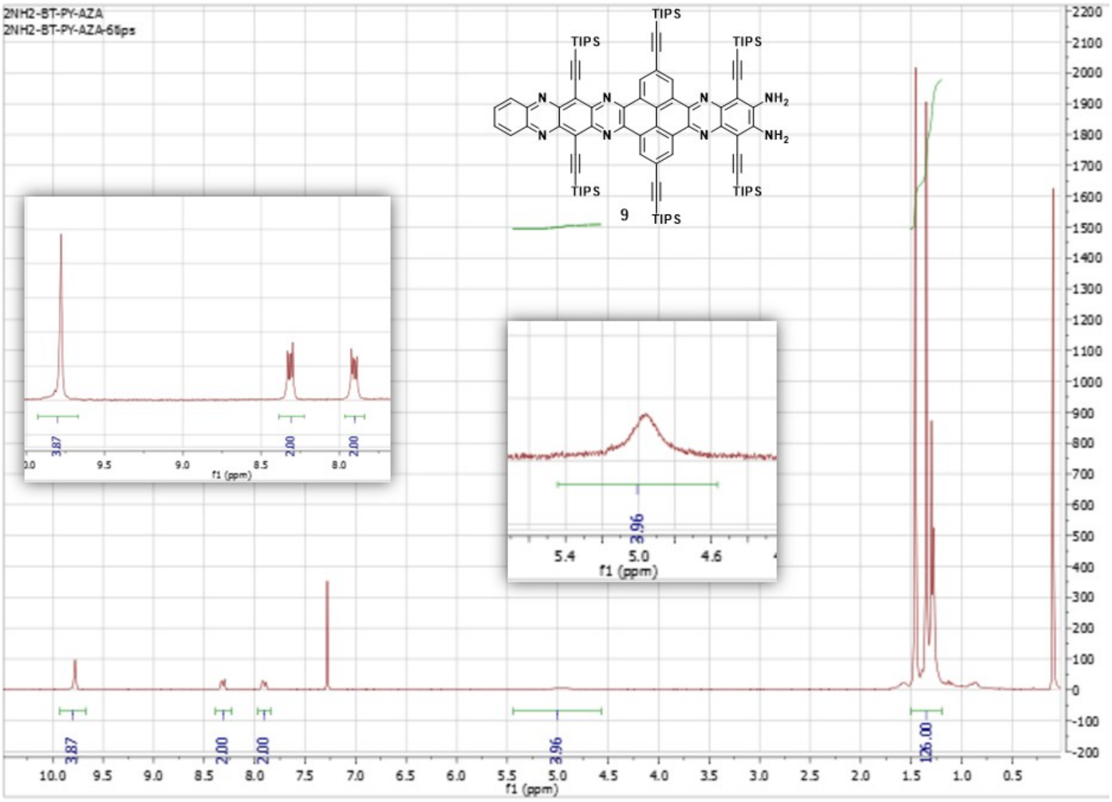


Figure S6. $^1$H NMR spectrum of compound **9**.

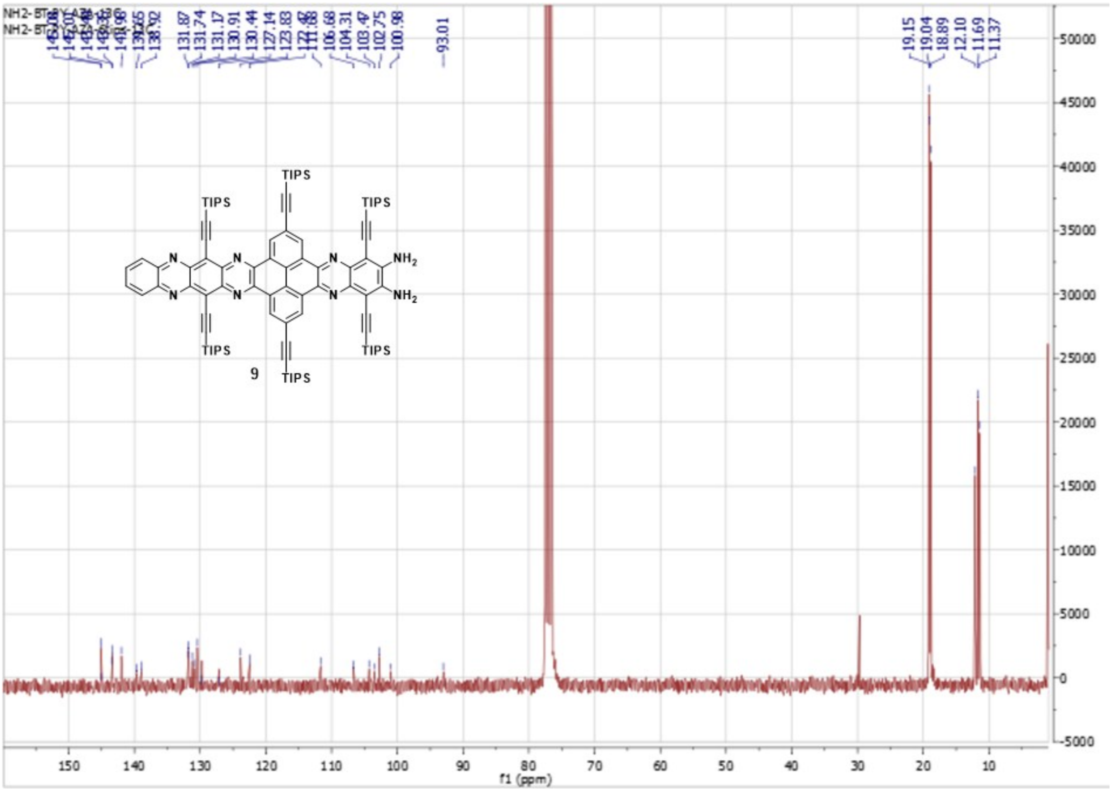


Figure S7. $^{13}$C NMR spectrum of compound **9**.

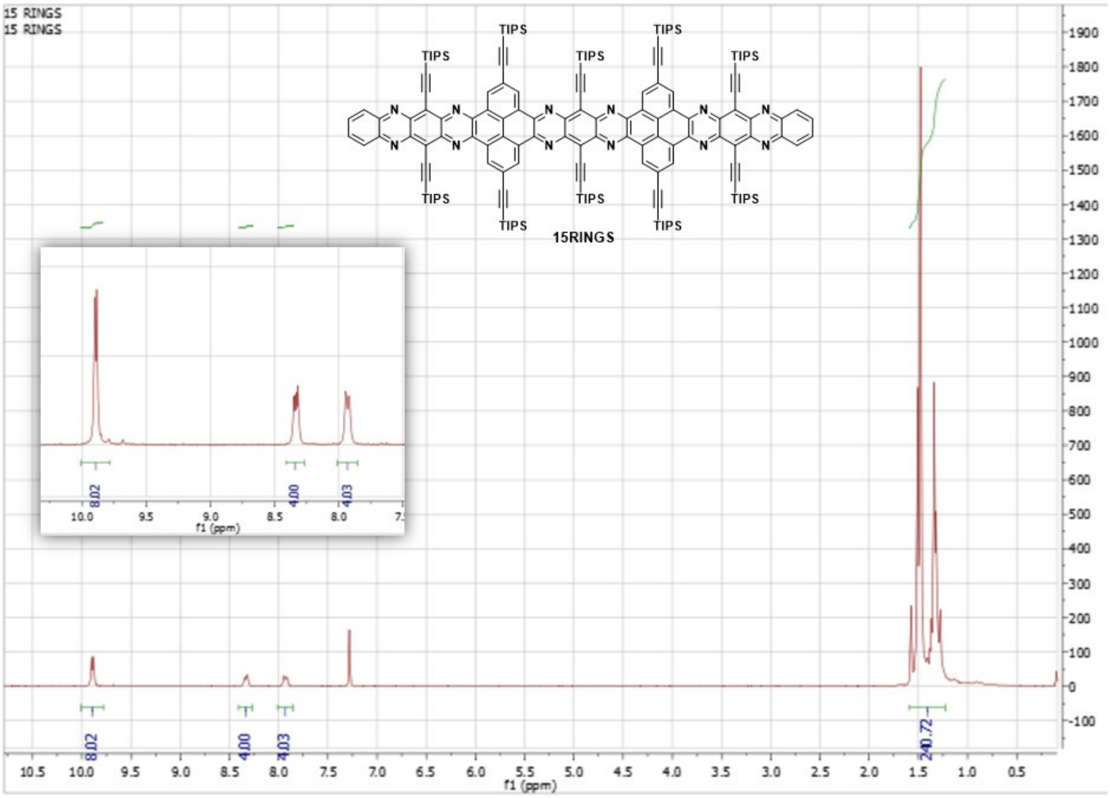


Figure S8. $^{1}$H NMR spectrum of compound **15RINGS**.

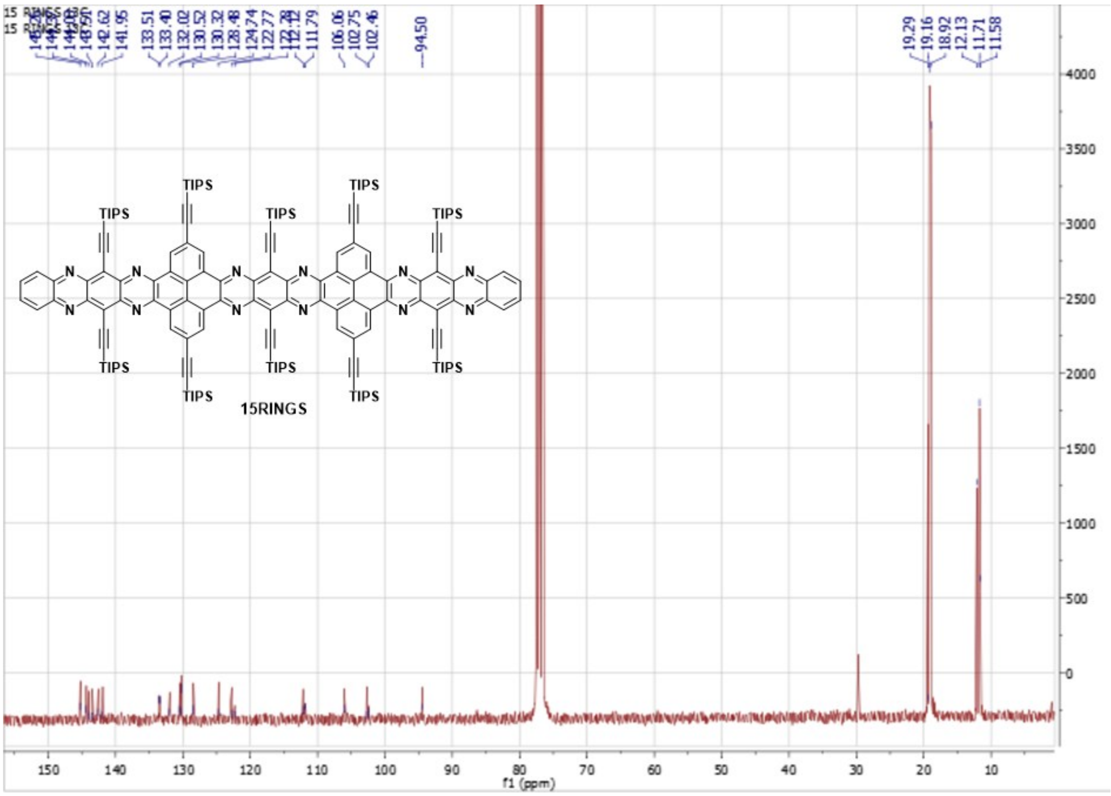
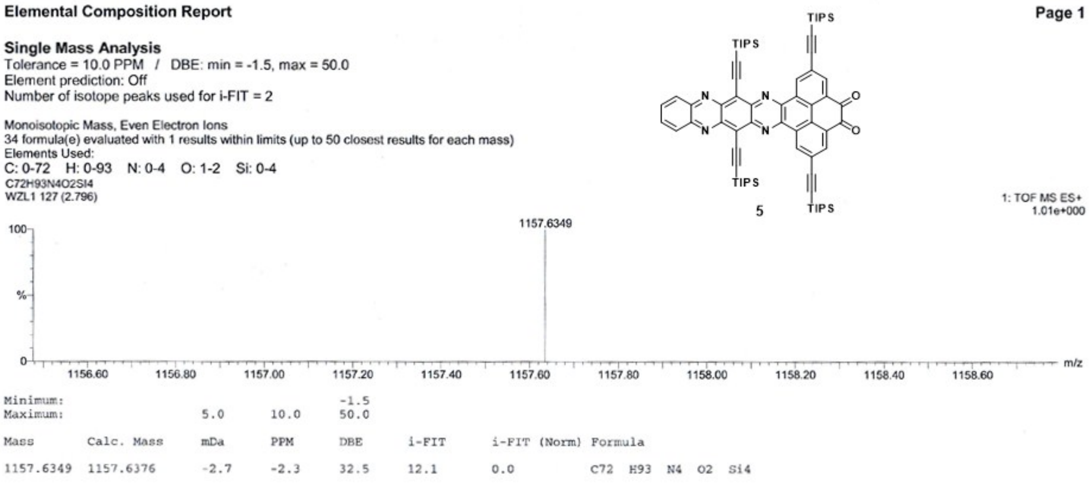


Figure S9. $^{13}$C NMR spectrum of compound **15RINGS**.



**Elemental Composition Report**

Page 1

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

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: 0-72 H: 0-93 N: 0-4 O: 1-2 Si: 0-4
C72H93N4O2Si4
WZL1 127 (2.796)

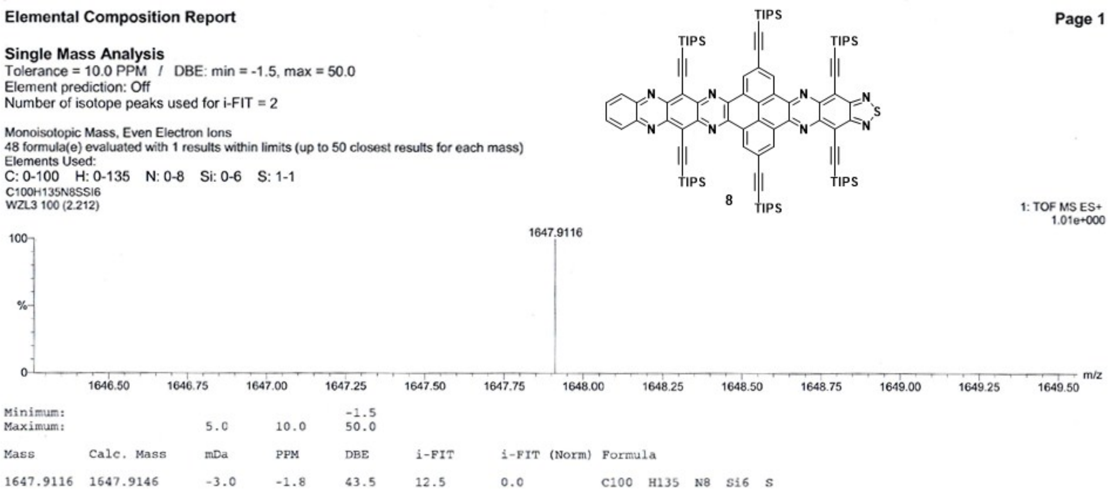
1: TOF MS ES+
1.01e+000

```
Minimum:                              -1.5
Maximum:              5.0     10.0    50.0

Mass       Calc. Mass  mDa    PPM     DBE    i-FIT   i-FIT (Norm) Formula

1157.6349  1157.6376   -2.7   -2.3    32.5   12.1    0.0          C72  H93  N4  O2  Si4
```

Figure S10. HR-MS spectrum of compound **5**.



**Elemental Composition Report**

Page 1

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-135 N: 0-8 Si: 0-6 S: 1-1
C100H135N8SSI6
WZL3 100 (2.212)

1: TOF MS ES+
1.01e+000

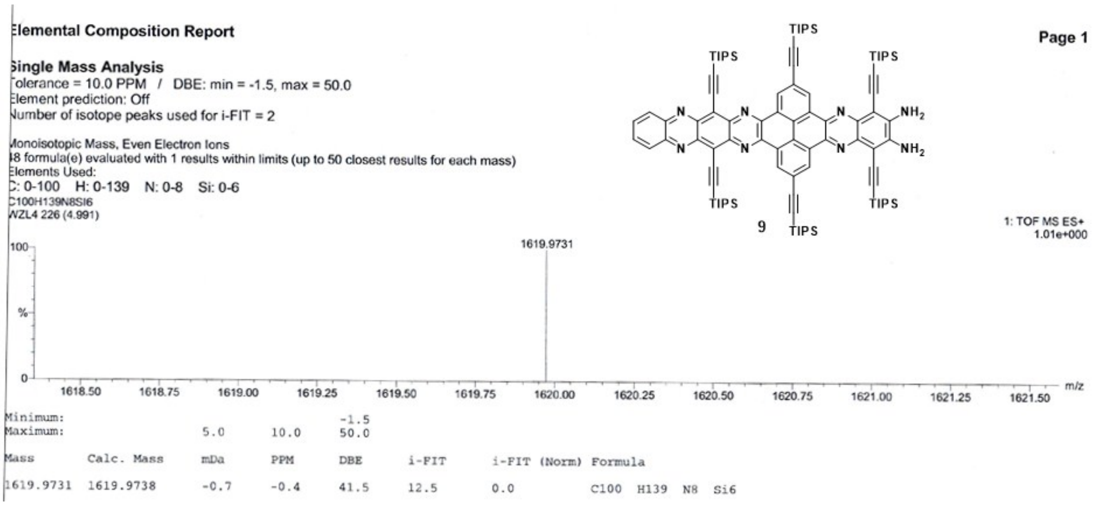
1647.9116

```
Minimum:                              -1.5
Maximum:              5.0     10.0    50.0

Mass       Calc. Mass  mDa     PPM     DBE     i-FIT     i-FIT (Norm) Formula

1647.9116  1647.9146   -3.0    -1.8    43.5    12.5      0.0          C100  H135  N8  Si6  S
```

Figure S11: HR-MS spectrum of compound **8**.



**Elemental Composition Report**

Page 1

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-139 N: 0-8 Si: 0-6
C100H139N8SI6
WZL4 226 (4.991)

1: TOF MS ES+
1.01e+000

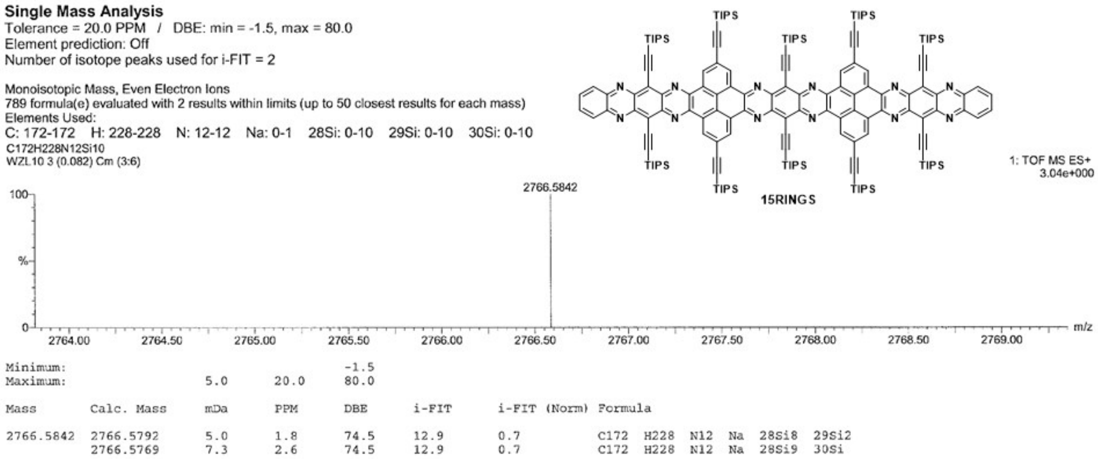
1619.9731

```
Minimum:                              -1.5
Maximum:              5.0     10.0    50.0

Mass       Calc. Mass  mDa     PPM     DBE     i-FIT     i-FIT (Norm) Formula

1619.9731  1619.9738   -0.7    -0.4    41.5    12.5      0.0          C100  H139  N8  Si6
```

Figure S12. HR-MS spectrum of compound **9**.



**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 80.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
789 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 172-172 H: 228-228 N: 12-12 Na: 0-1 28Si: 0-10 29Si: 0-10 30Si: 0-10
C172H228N12Si10
WZL10 3 (0.082) Cm (3:6)

1: TOF MS ES+
3.04e+000

2766.5842

```
Minimum:                              -1.5
Maximum:              5.0     20.0    80.0

Mass       Calc. Mass  mDa     PPM     DBE     i-FIT     i-FIT (Norm) Formula

2766.5842  2766.5792   5.0     1.8     74.5    12.9      0.7          C172  H228  N12  Na  28Si8  29Si2
           2766.5769   7.3     2.6     74.5    12.9      0.7          C172  H228  N12  Na  28Si9  30Si
```

Figure S13. HR-MS spectrum of compound **15RINGS**.

## 6. Femtosecond transient absorption spectra

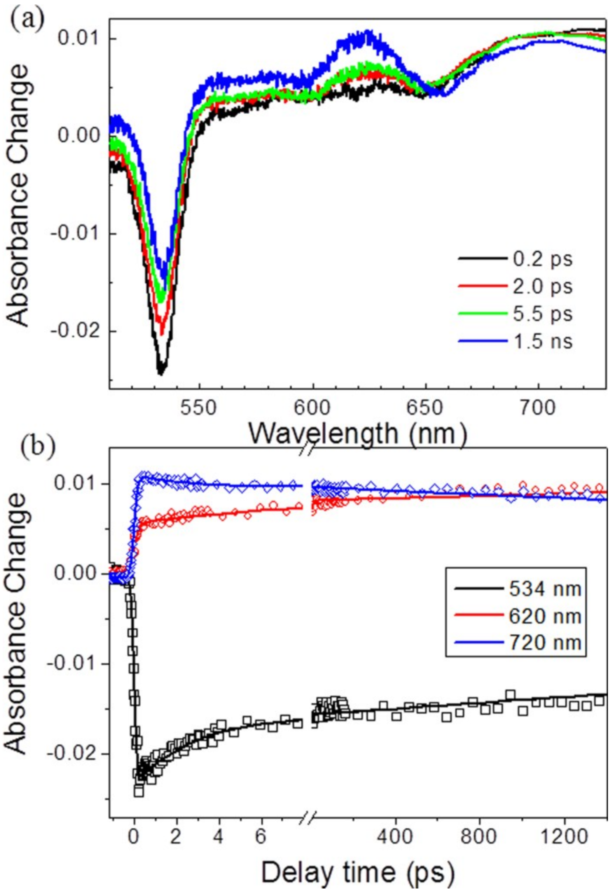


Figure S14. Femtosecond transient absorption spectra (a) and the representative kinetic curves (open symbols) as well as the correspond fits (solid lines) (b) of **15RINGS** in dichloromethane solution.

Figure S14 shows the femtosecond transient absorption spectra of **15RINGS** solution (dichloromethane) upon excitation at 480 nm, which triggers the S2←S0 transition. Photoexcitation of **15RINGS** immediately produces a strong negative band at 534 nm owing to ground state bleaching (GSB) along with a broad positive excited state absorption band peaked at 730 nm. As time proceeds, the band at 730 nm decays and slightly blue-shifts. Simultaneously, a new spectral feature at 620 nm gradually appears and dominates at ~1.5 ns. We assign the long-lived absorption band to be the triplet state via intersystem crossing (ISC). The GSB signal decays bi-exponentially with two components of 3.0±0.8 ps and 28±8 ns. Analysis of the 620-nm curve results in one rising lifetime of 1.0±0.2 ns (red line in Figure S14b), suggesting the rate constant of $1.0\times10^{9}$ $s^{-1}$ for ISC process.

## Reference:

1. G. M. Sheldrick, *Acta Crystallographica Section A: Foundations of Crystallography*, **2008**, *64*, 112-122.