Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Structure Engineering: Extending the Length of Azaacenes Derivatives through Quinone Bridge

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Table of Content

Experimental methods and instruments

Materials

All the chemicals and solvents are purchased and used without further treatment unless special note. Chloroform and *N*,*N*-Diisopropylethylamine (Hünig's base) 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. The 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.

Single-crystal X-ray diffraction

The suitable black block-shaped single-crystals of Hex-CO and Hept-CO were selected for single-crystal X-ray data collection with a Bruker SMART APEXII CCD area detector on a D8 goniometer at 90-100 K. Data were collected using graphite-monochromated and 0.5 mm-Mono Cap-collimated Mo-Kα radiation (λ = 0.71073 Å) with the ω scan method. The data were processed with the INTEGRATE program of the APEX3 software for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for area detector. The Structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 (SHELX-97).[1] All non-H atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included as riding with U_{iso} (H) = 1.2 U_{eq} (C).

Synthesis details

Synthesis of 6,17-bis((triisopropylsilyl)ethynyl)naphtho[2,3-b]quinoxalino[2,3-i]phenazine-8,15(7H,16H)-dione (Compound 5)

The diamine compound **1** (114 mg, 0.2 mmol), dichloride compound **2** (125 mg, 0.45 mmol), 2-dicyclohexylphosphino-2’,6’-diisopropoxybiphenyl (RuPhos) (7 mg, 0.015 mmol), Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (14 mg, 0.015 mmol), dry Hünig's base (5 mL) and dry chloroform (20 mL) were added into the Schlenk flask under argon atmosphere. Subsequently, the mixture was further bubbled with argon for 5 min to remove the oxygen. Then, the solution was stirred at 70 ºC for 48 h. After the mixture was cooled to room temperature, it was filtered on celite and washed with methylene chloride until the filtrate is colorless. The filtrate was washed with saturated ammonium chloride solution and extracted with methylene chloride. After the organic layer was collected and dried with Na_2SO_4, followed by filtration and the removing of solvents, the residue was purified by silica gel column chromatography (Eluent: CH_2Cl_2 : Hex = 1 : 3). The as-obtained crude product was dissolved in small amount $CHCl_3$ and reprecipitated by adding methanol. The solid was collected by filtration and washed with methanol to afford pure compound **5** (115 mg, 0.15 mmol, 74%) as brown solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 2H), 8.04 – 7.83 (m, 4H), 7.73 – 7.41 (m, 6H), 1.45 – 1.14 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.88, 144.10, 142.41, 138.02, 134.70, 130.13, 129.57, 129.16, 129.08, 128.61, 126.98, 126.26, 106.27, 101.19, 97.96, 18.88, 11.42. HR-MS (ESI) m/z Calc. for $[M+H]^+$ $C_{48}H_{55}N_4O_2Si_2$: 775.3864, found : 775.3848.

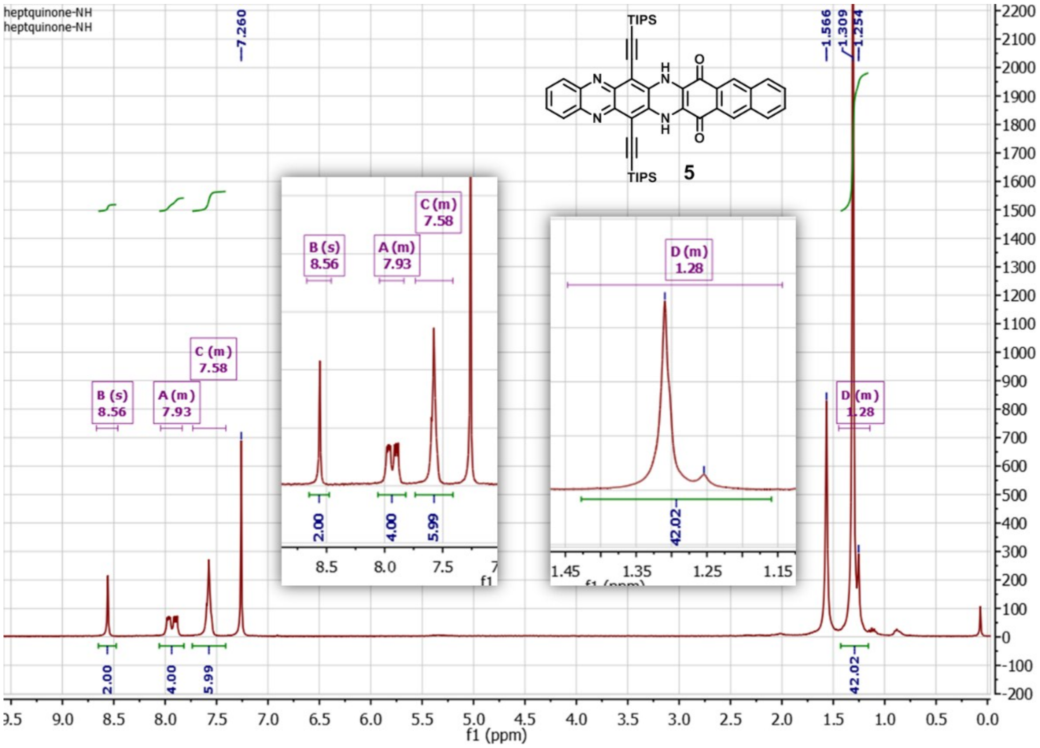


Figure S1. ^{1}H NMR spectrum of compound **5**

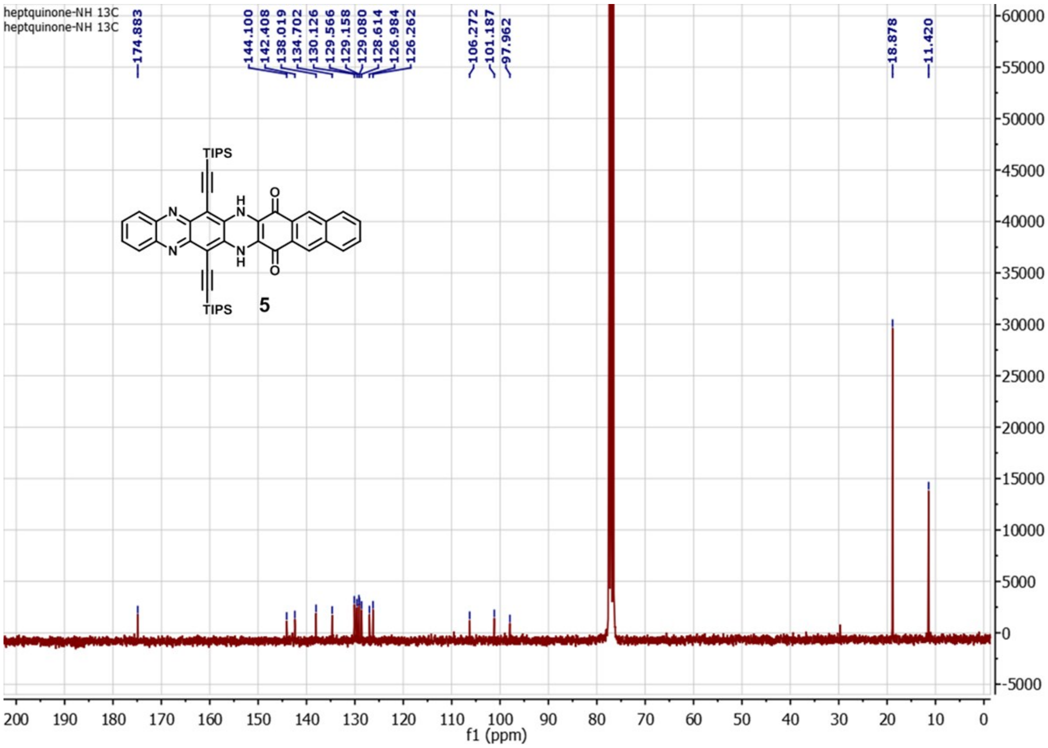
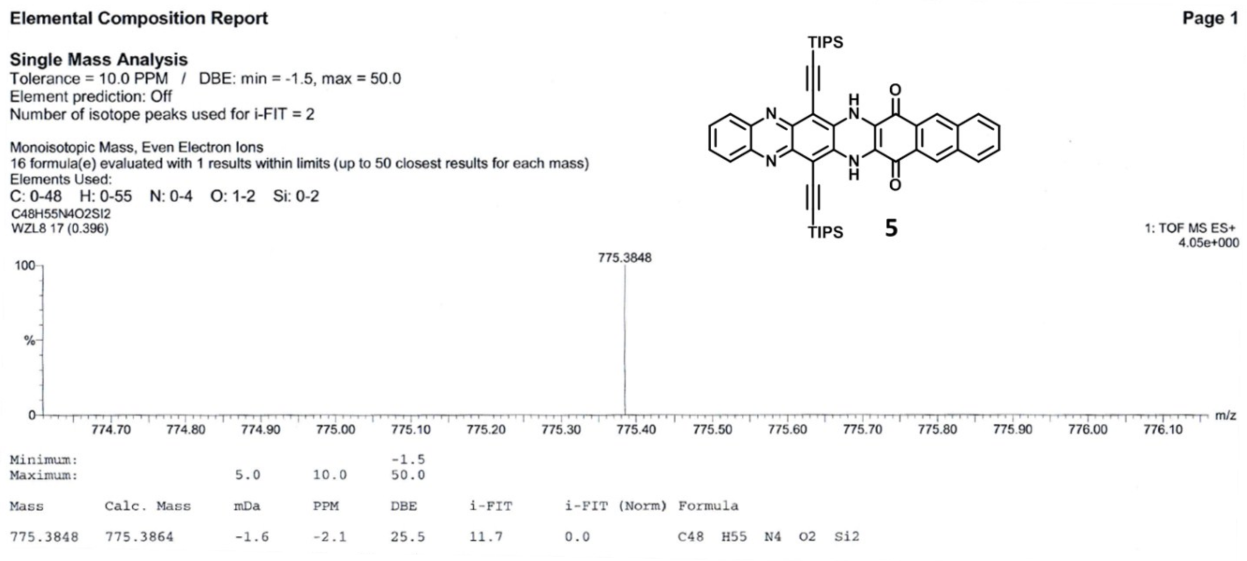


Figure S2. ^{13}C NMR spectrum of compound **5**



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
16 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-48 H: 0-55 N: 0-4 O: 1-2 Si: 0-2
C48H55N4O2SI2
WZL8 17 (0.396)

1: TOF MS ES+
4.05e+000

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Minimum:                              -1.5
Maximum:                5.0    10.0   50.0

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

775.3848  775.3864      -1.6   -2.1   25.5   11.7     0.0          C48  H55  N4  O2  Si2
```

Figure S3. HR-MS spectrum of compound **5**

6,15-bis((triisopropylsilyl)ethynyl)benzo[b]quinoxalino[2,3-i]phenazine-8,13(7H,14H)-dione (Compound 6)

Compound **6** was synthesized according to the same procedure for the preparation of compound **5**, by using compound **1** (114 mg, 0.2 mmol), dichloride compound **3** (103 mg, 0.45 mmol), RuPhos (7 mg, 0.015 mmol), $Pd_2(dba)_3$ (14 mg, 0.015mmol), dry Hünig's base (5 mL) and dry chloroform (15 mL). Compound **6** (120 mg, 0.17 mmol, 85%) was obtained as brown solid. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.12 – 8.01 (m, 2H), 7.94 – 7.84 (m, 2H), 7.73 – 7.64 (m, 2H), 7.63 – 7.52 (m, 2H), 7.49 (s, 2H), 1.31 – 1.20 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.68, 144.18, 142.40, 138.23, 133.79, 130.37, 129.15, 129.08, 126.18, 124.78, 106.28, 101.13, 97.99, 18.85, 11.39. HR-MS (ESI) m/z Calc. for $[M+H]^+$ $C_{44}H_{53}N_4O_2Si_2$: 725.3707, found : 725.3674.

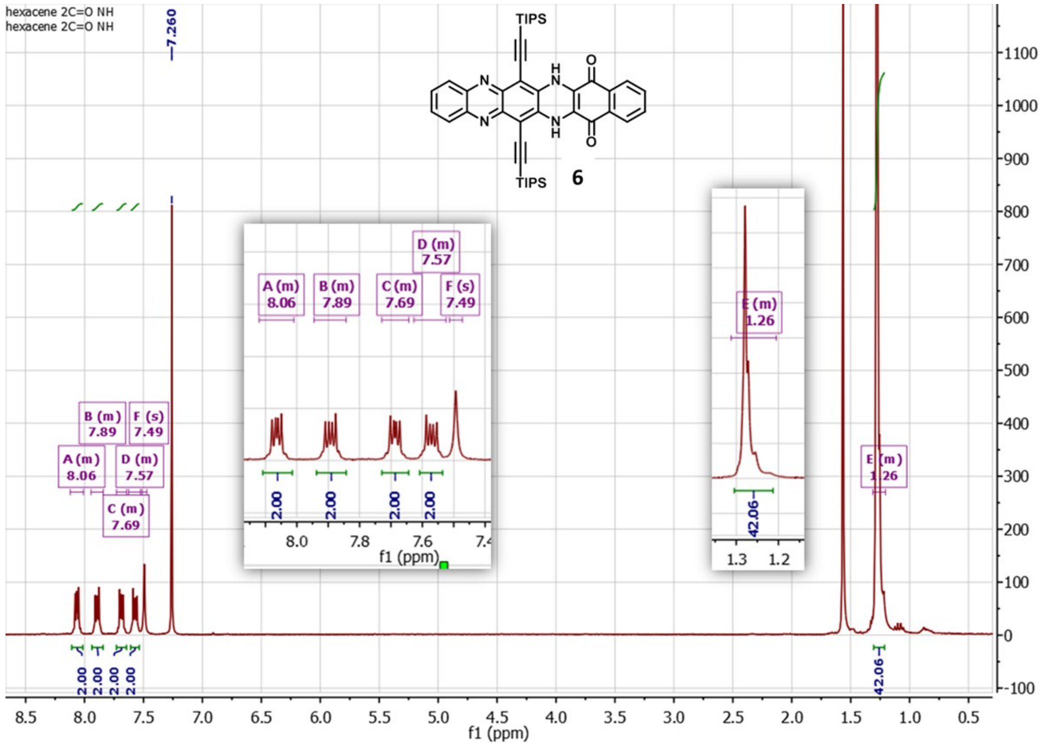


Figure S4. ^{1}H NMR spectrum of compound **6**

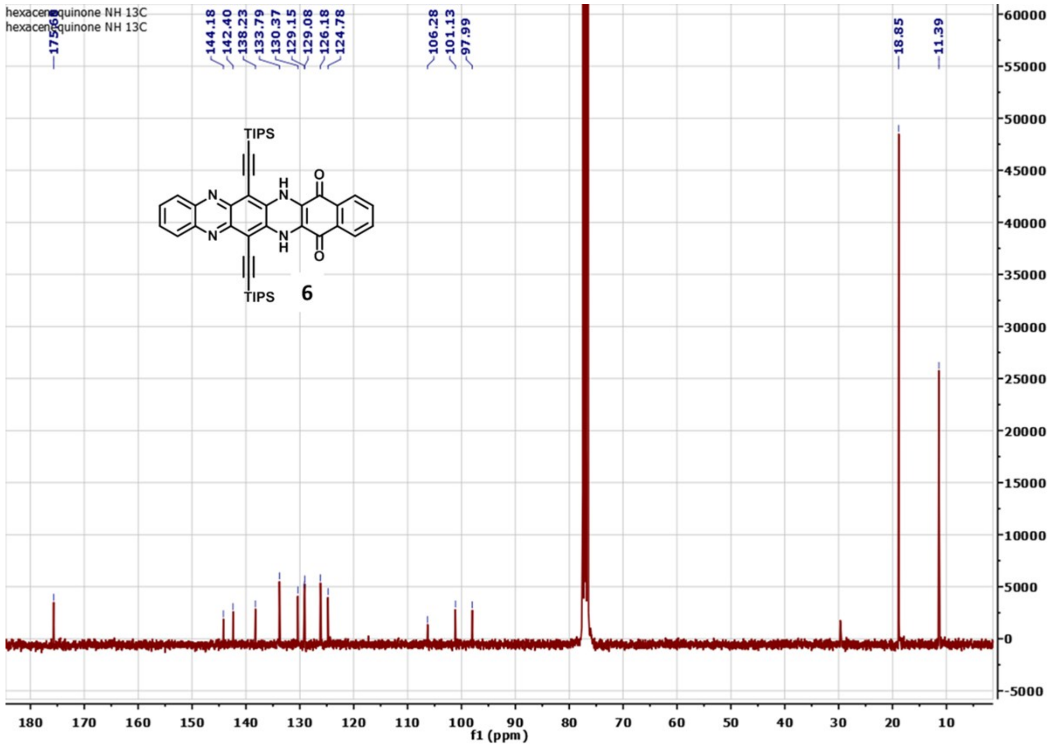
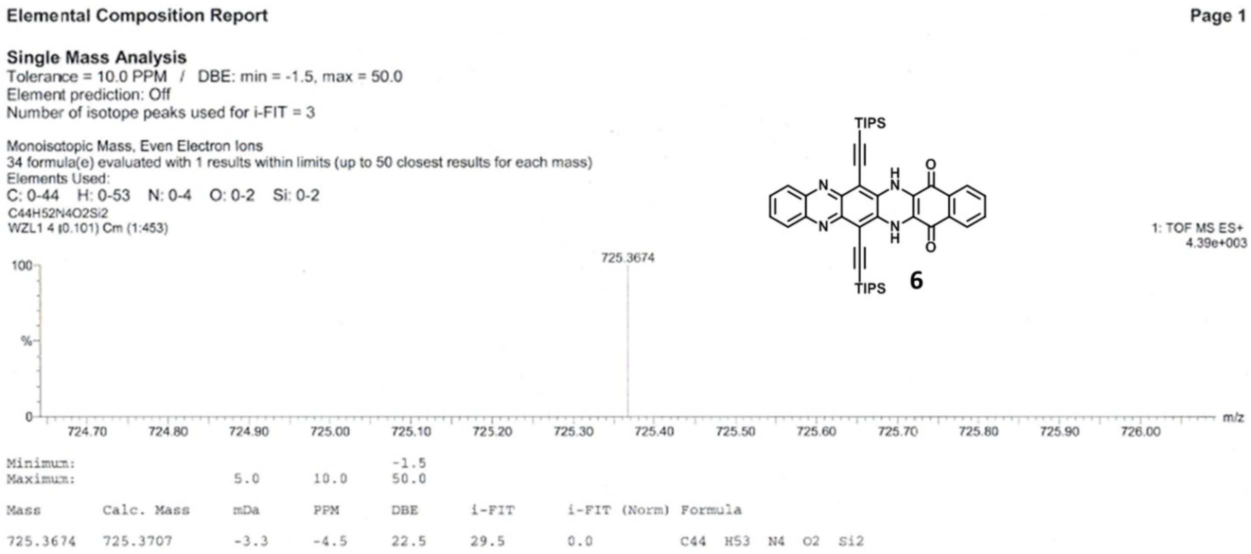


Figure S5. ^{13}C NMR spectrum of compound **6**



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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 = 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: 0-44   H: 0-53   N: 0-4   O: 0-2   Si: 0-2
C44H52N4O2Si2
WZL1 4 (0.101) Cm (1:453)

Minimum:                                 -1.5
Maximum:                  5.0     10.0    50.0

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

725.3674  725.3707       -3.3     -4.5    22.5     29.5     0.0          C44  H53  N4  O2  Si2
```

Figure S6. HR-MS spectrum of compound **6**

1-chloro-6,13-bis((triisopropylsilyl)ethynyl)-6a,7,12,12a-tetrahydroquinoxalino[2,3-b]phenazin-2(14H)-one (Compound 8)

Compound **8** was synthesized according to the same procedure for the preparation of compound **5**, by using compound **1** (114 mg, 0.2 mmol), dichloride compound **4** (80 mg, 0.45 mmol), RuPhos (7 mg, 0.015 mmol), $Pd_2(dba)_3$ (14 mg, 0.015mmol), dry Hünig's base (5 mL) and dry chloroform (10 mL). Compound **8** (43 mg, 0.06 mmol, 31%) was obtained as orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.76 (d, *J*=9.0, 1H), 7.32 (d, *J*=9.0, 1H), 7.14 (s, 1H), 7.02 (s, 1H), 6.88 – 6.64 (m, 2H), 6.59 – 6.33 (m, 2H), 6.07 (s, 1H), 1.34 – 1.17 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.68, 143.61, 142.12, 140.38, 139.25, 138.99, 138.37, 128.69, 128.36, 128.06, 123.54, 123.31, 119.54, 113.93, 113.81, 112.91, 104.66, 104.51, 99.40, 99.25, 96.91, 96.76, 18.93, 18.89, 11.43, 11.42.

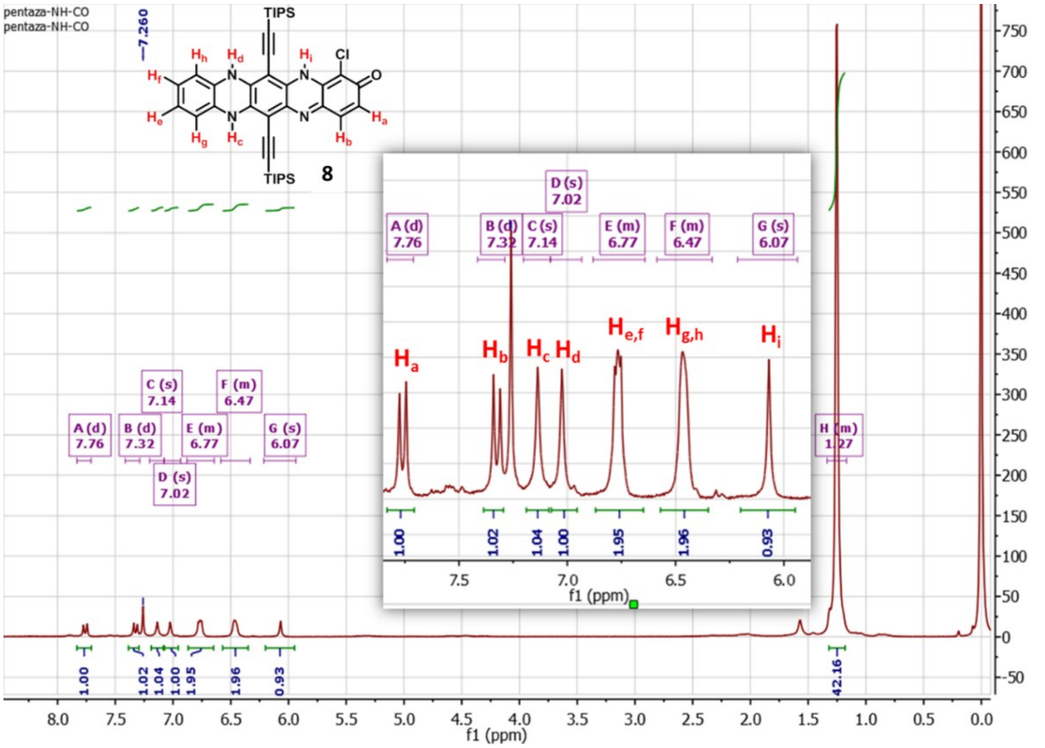


Figure S7. ^{1}H NMR spectrum of compound **8**

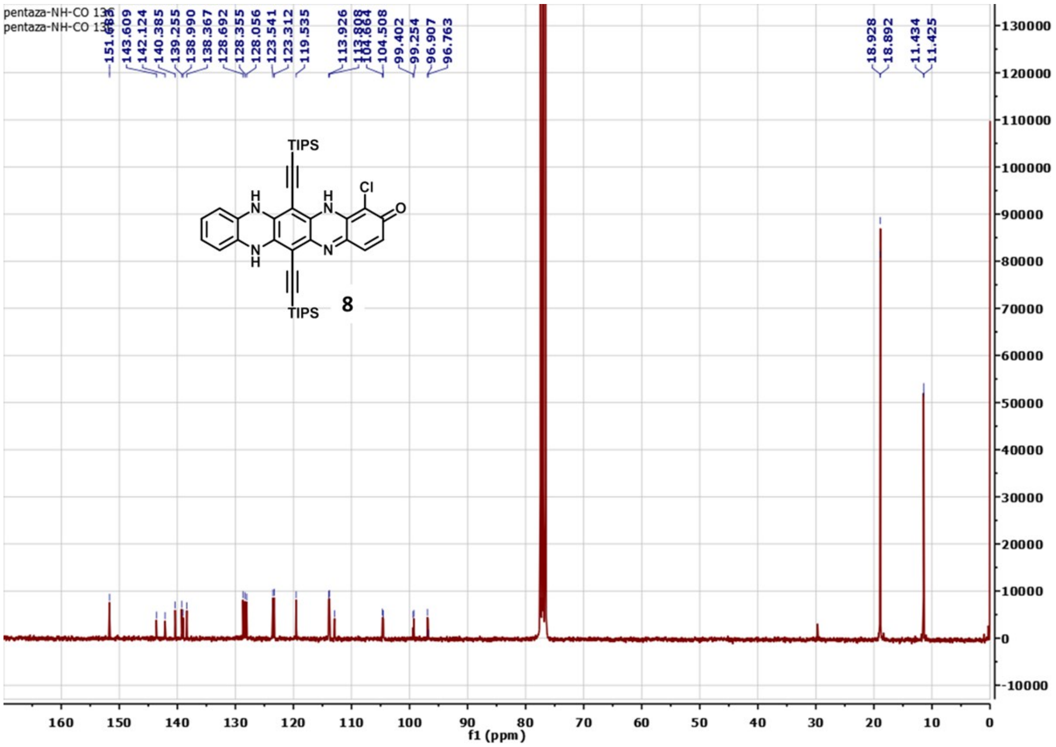
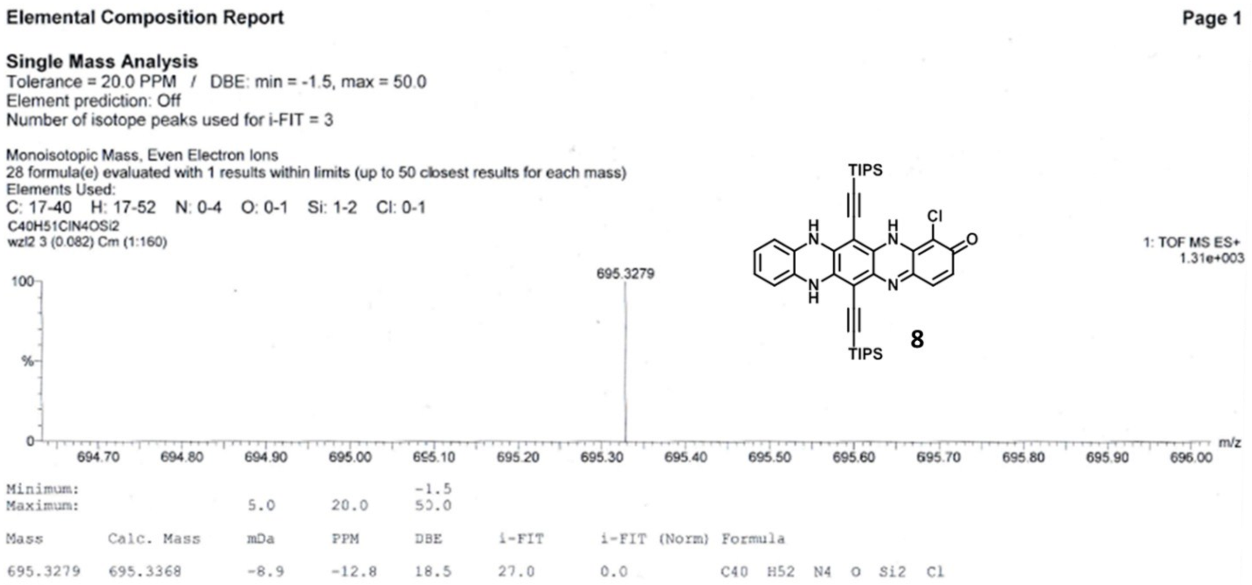


Figure S8. ^{13}C NMR spectrum of compound **8**



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Elemental Composition Report                                                    Page 1

Single Mass Analysis
Tolerance = 20.0 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
28 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-40   H: 17-52   N: 0-4   O: 0-1   Si: 1-2   Cl: 0-1
C40H51ClN4OSi2
wzl2 3 (0.082) Cm (1:160)

Minimum:                                      -1.5
Maximum:                    5.0      20.0     50.0

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

695.3279   695.3368        -8.9     -12.8     18.5     27.0       0.0          C40  H52  N4  O  Si2  Cl
```

Figure S9. HR-MS spectrum of compound 8

6,17-bis((triisopropylsilyl)ethynyl)naphtho[2,3-b]quinoxalino[2,3-i]phenazine-8,15-dione (Hept-CO)

Compound **5** (50 mg, 0.06 mmol) was treated with excess amount active MnO_2 in dry methylene chloride (20 mL) at room temperature for about 2 h. The solution turned to dark green, immediately. The completion of the reaction was confirmed by thin layer chromatography (TLC). Subsequently, MnO_2 was removed by filtration through celite and washed with methylene chloride until the filtrate was colorless. After removing the solvent, the solid was dissolved in small amount diethyl ether and reprecipitated by adding methanol. The solid was collected by filtration and washed with methanol to afford pure **Hept-CO** (32 mg, 0.04 mmol, 65%) as black solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.13 (s, 2H), 8.33 – 8.23 (m, 2H), 8.23 – 8.14 (m, 2H), 7.97 – 7.87 (m, 2H), 7.86 – 7.72 (m, 2H), 1.49 – 1.26 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 180.21, 145.93, 145.71, 144.14, 142.36, 135.67, 132.94, 131.17, 130.64, 130.40, 130.37, 130.32, 125.75, 115.45, 101.65, 18.94, 11.71. HR-MS (ESI) m/z Calc. for $[M+H]^+$ $C_{48}H_{53}N_4O_2Si_2$: 773.3707, found : 773.3686.

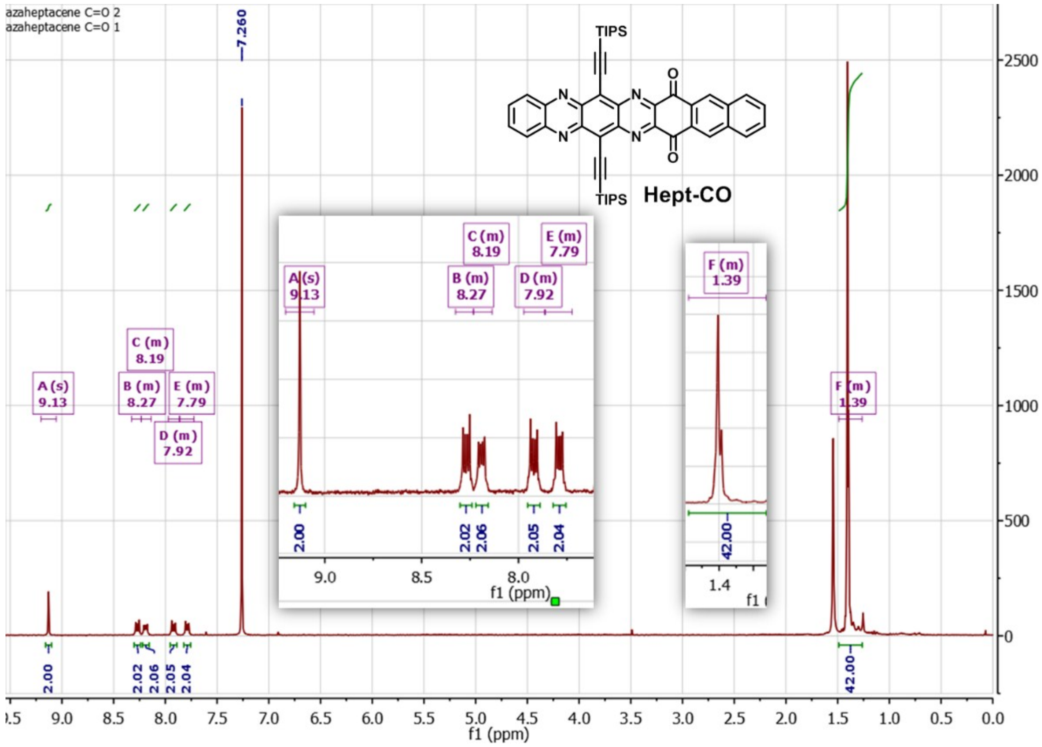


Figure S10. ^{1}H NMR spectrum of compound **Hept-CO**

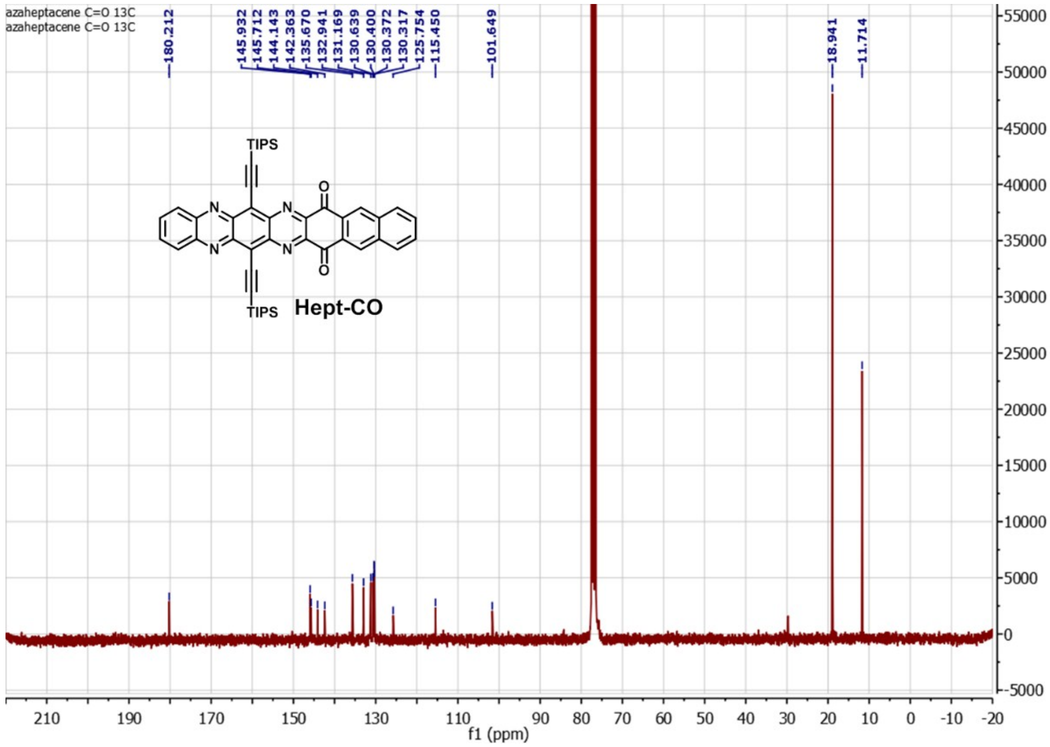
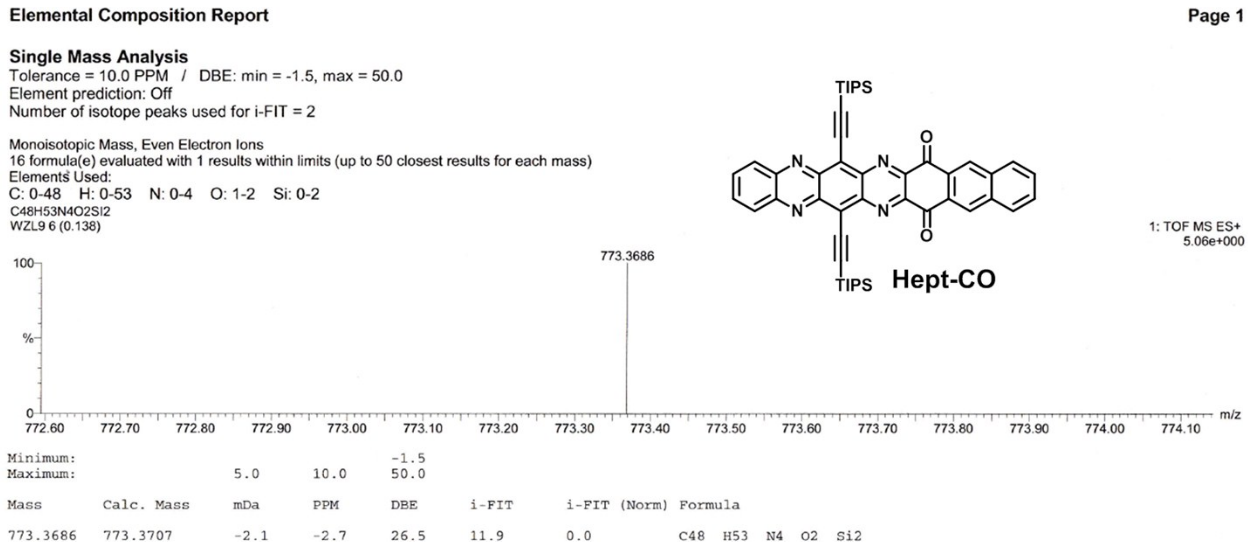


Figure S11. ^{13}C NMR spectrum of compound **Hept-CO**



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
16 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-48 H: 0-53 N: 0-4 O: 1-2 Si: 0-2
C48H53N4O2Si2
WZL9 6 (0.138)

1: TOF MS ES+
5.06e+000

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

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

773.3686   773.3707       -2.1     -2.7    26.5     11.9      0.0          C48  H53  N4  O2  Si2
```

Figure S12. HR-MS spectrum of compound **Hept-CO**

6,15-bis((triisopropylsilyl)ethynyl)benzo[b]quinoxalino[2,3-i]phenazine-8,13-dione (Hex-CO)

Hex-CO was synthesized according to the same procedure for the preparation of **Hept-CO**, by using compound **6** (50 mg, 0.07 mmol). Pure **Hex-CO** (28 mg, 0.04 mmol, 56%) was obtained as black solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.60 – 8.50 (m, 2H), 8.31 – 8.22 (m, 2H), 8.00 – 7.88 (m, 4H), 1.46 – 1.27 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 180.04, 145.87, 145.04, 144.07, 142.27, 135.23, 134.63, 132.96, 130.57, 128.47, 125.78, 115.44, 101.52, 18.92, 11.69.

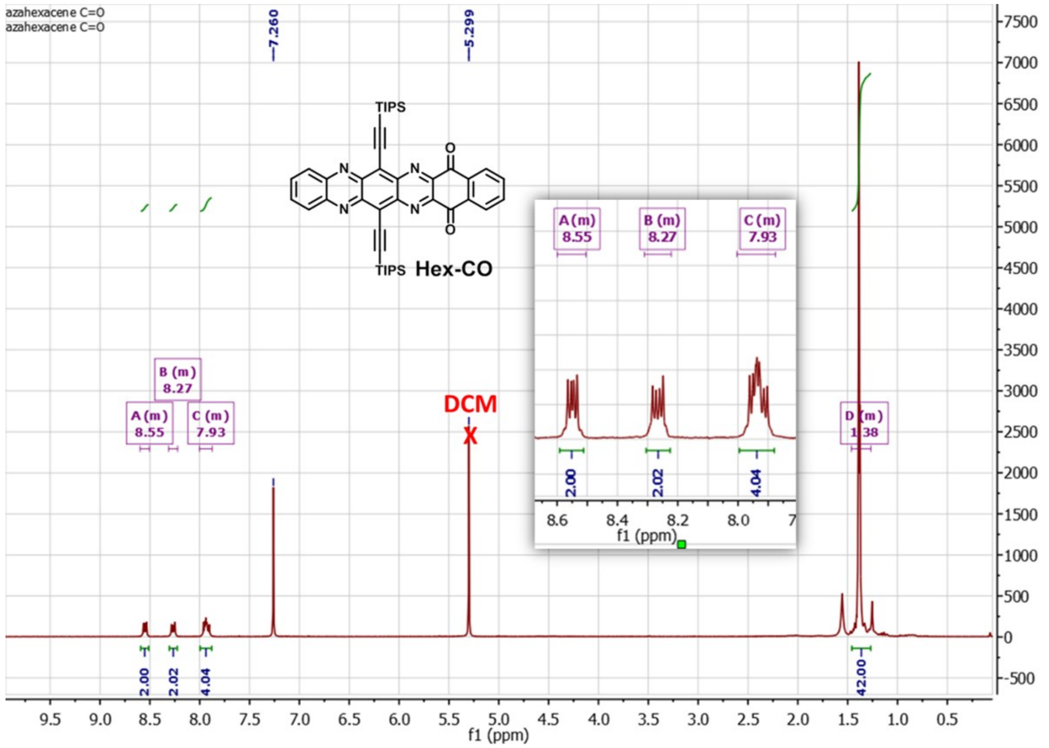


Figure S13. ^{1}H NMR spectrum of compound **Hex-CO**

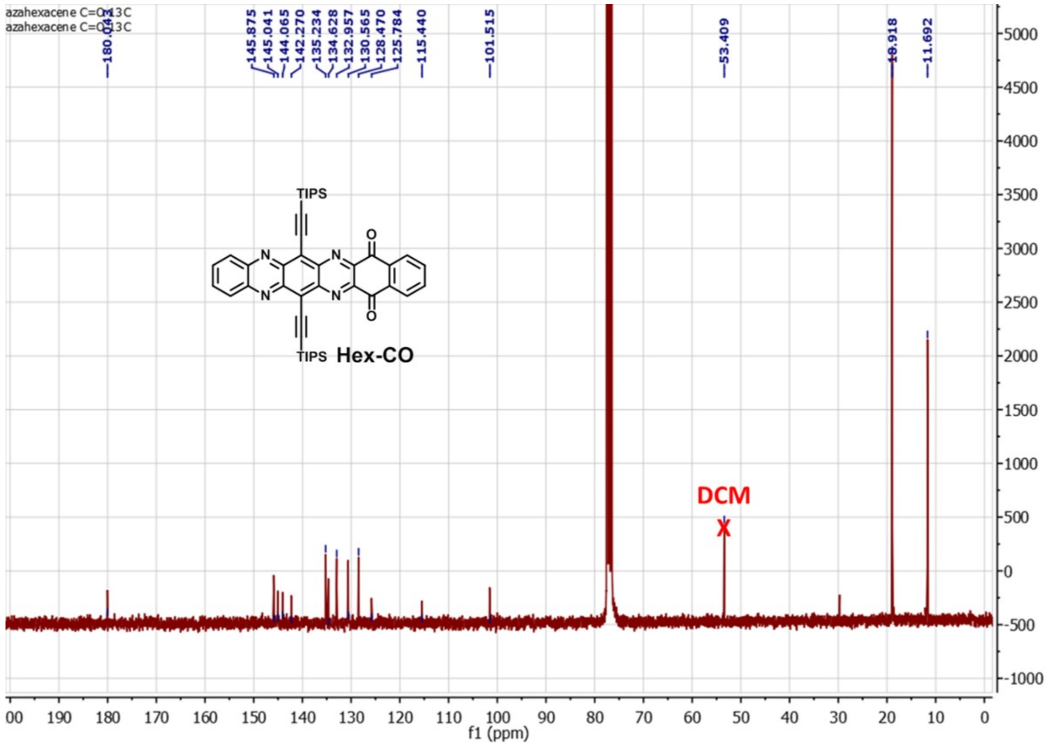
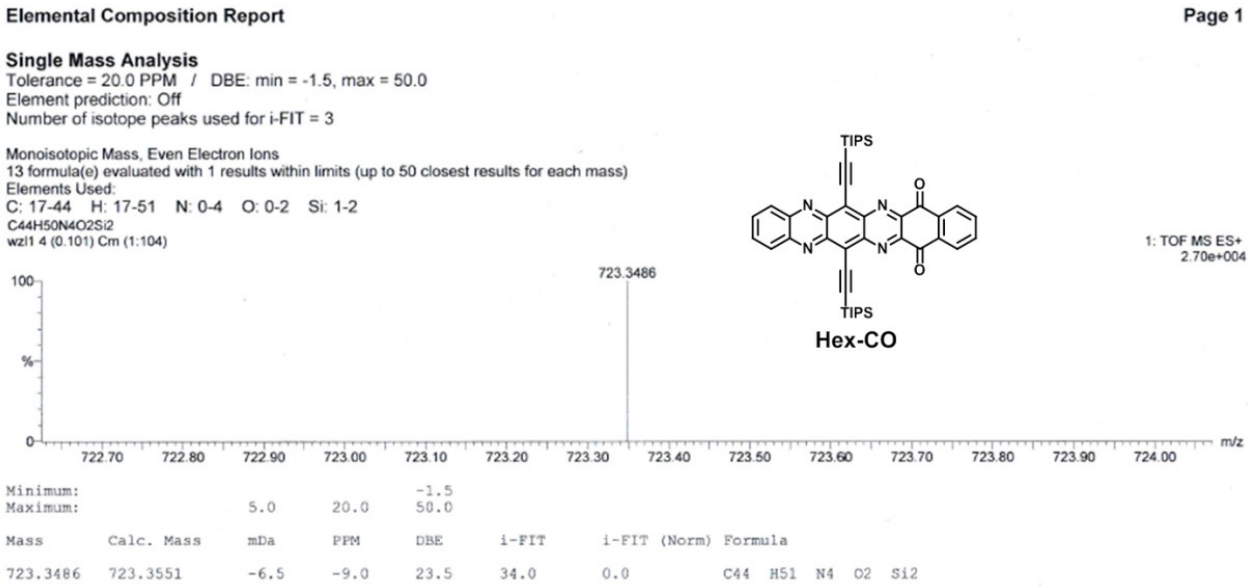


Figure S14. ^{13}C NMR spectrum of compound **Hex-CO**



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Elemental Composition Report                                                    Page 1

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 17-44    H: 17-51    N: 0-4    O: 0-2    Si: 1-2
C44H50N4O2Si2
wzl1 4 (0.101) Cm (1:104)                                                1: TOF MS ES+
                                                                              2.70e+004

Minimum:                                     -1.5
Maximum:                      5.0     20.0   50.0

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

723.3486    723.3551      -6.5    -9.0    23.5    34.0      0.0          C44  H51  N4  O2  Si2
```

Figure S15. HR-MS spectrum of compound **Hex-CO**

Supporting Figures

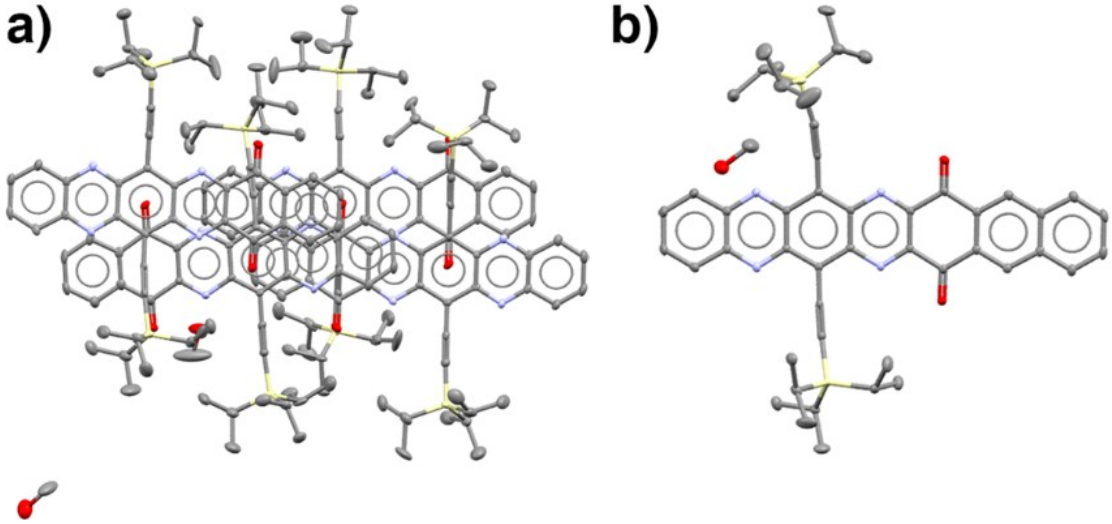

Figure S16. Molecular crystal structures of **Hex-CO** (a) and **Hept-CO** (b) with 50% probability ellipsoid. Colour scheme: C, gray; N, blue; Si, yellow; O, red. H atoms are omitted for clarity.

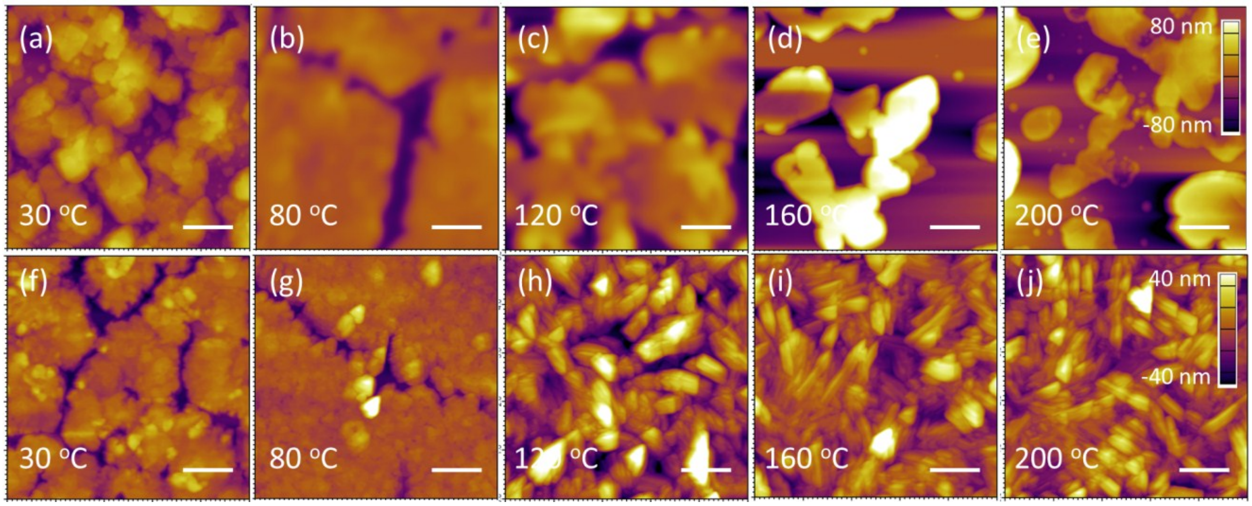

Figure S17. AFM images of thin films of (a-e) compounds **Hex-CO** and (f-j) **Hept-CO** at different annealing temperatures

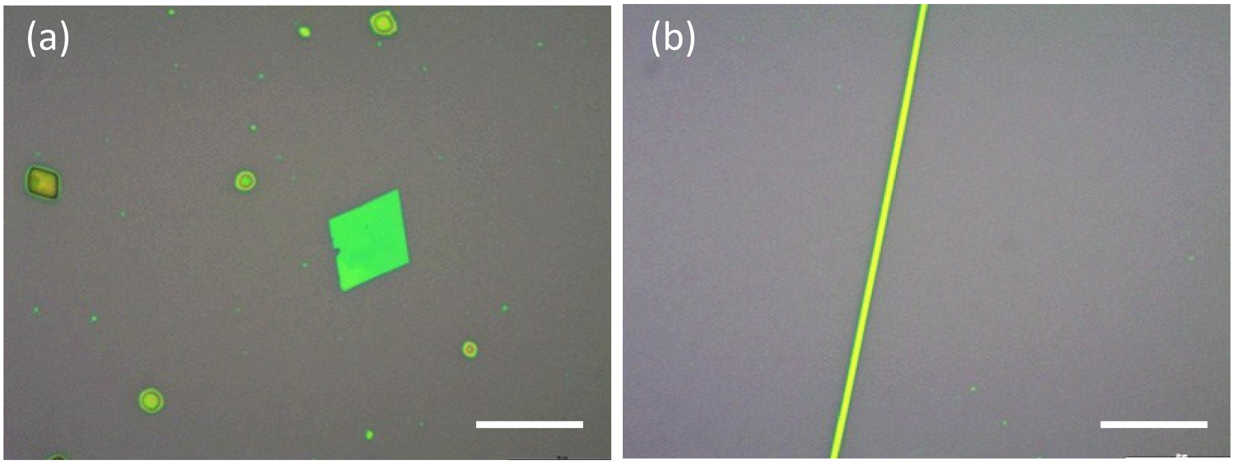

Figure S18. Images of the as-casted micro crystals of (a) **Hex-CO** and (b) **Hept-CO** (scale bar: 20 μm).

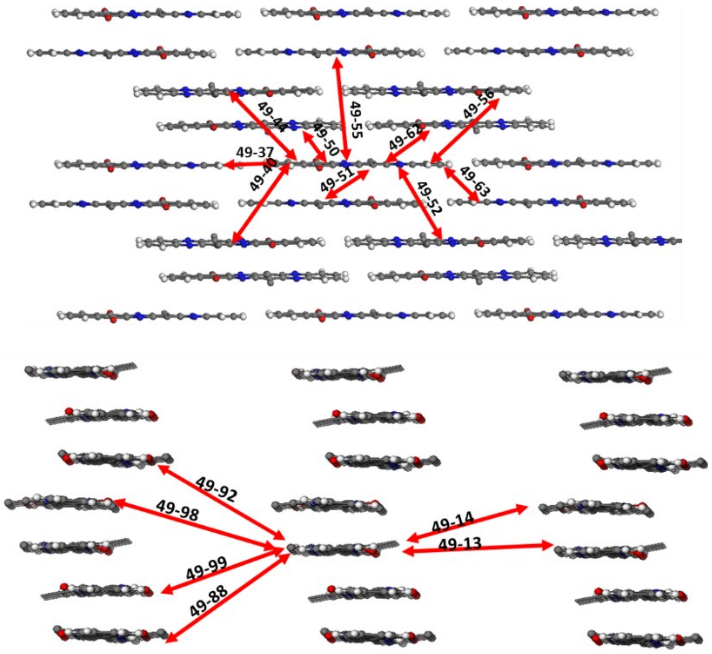

Figure S19. Hoping route of **Hex-CO** in the crystal (the hydrogen atoms are omitted for clarification); The intermolecular electronic couplings of hole transfer (V_h) and electron transfer (V_e) for the center molecule **49** are calculated at DFT/B3LYP/6-31G(d) level, which were obtained through a direct evaluation of the coupling element between frontier orbitals using the unperturbed density matrix of the dimer Fock operator[2,3]

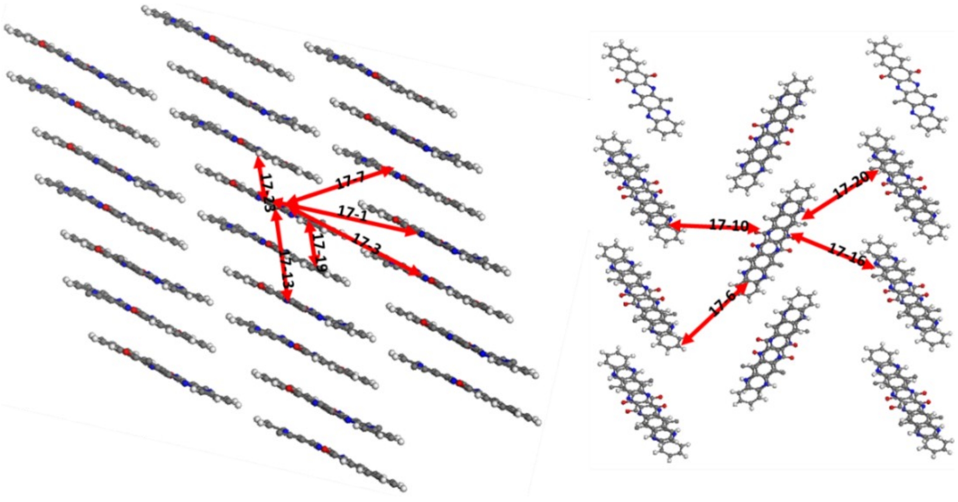

Figure S20. Hoping route of **Hept-CO** in the crystal (the hydrogen atoms are omitted for clarification); The intermolecular electronic couplings of hole transfer (V_h) and electron transfer (V_e) for the center molecule **17** are calculated at DFT/B3LYP/6-31G(d) level, which were obtained through a direct evaluation of the coupling element between frontier orbitals using the unperturbed density matrix of the dimer Fock operator[2,3]

Supporting Tables

Table S1. Crystallographic data and structure refinement parameters of **Hex-CO and Hept-CO**

	Hex-CO	**Hept-CO**
CCDC number	1577484	1577485
T (K)	90	100
Formula	$C_{89} H_{104} N_8 O_5 Si_4$	$C_{49} H_{56} N_4 O_3 Si_2$
Formula weight	1478.16	805.15
Crystal system	Triclinic	Monoclinic
Space group	*P*	$P2_1$/c
a (Å)	21.5519（19）	12.3896 (17)
b (Å)	21.7004（18））	13.6687 (19)
c (Å)	22.1556（19）	23.797 (3)
α (deg)	63.925 (2)	90
β (deg)	85.605 (2)	95.3293 (7)
γ (deg)	63.452 (2)	90
V (Å^3)	8232.8 (12)	4354.78 (16)
λ (Mo Kα) (Å)	0.71073	0.71073
Collected reflns	44233	32275
Unique reflns	28625	8878
Parameters	1962	538
R (int)	0.0536	0.0359
R_1 [$I > 2\sigma(I)$]	0.0838	0.0542
wR_2 [$I > 2\sigma(I)$]	0.2079	0.1217
GOF	1.059	1.015

Table S2. The electronic couplings for all the hopping pathways of **Hex-CO**

Pathway	center-center/Å	V_h/meV	V_e/meV
49-13	18.54000	-0.05264	-0.01507
49-14	18.23855	0.06780	0.01242
49-37	18.32299	0.00187	2.75964
49-40	14.64957	0.00004	-0.01632
49-44	15.11292	0.00003	-0.01906
49-50	9.59044	8.03378	33.09652
49-51	6.42003	1.24167	64.90778
49-52	8.72079	1.05133	0.15240
49-55	10.22879	0.01801	-0.00035
49-56	8.89166	0.02832	0.03702
49-62	9.19673	23.62718	61.70732
49-63	15.19850	0.08386	13.70639
49-88	16.51413	6.33952	0.12215
49-92	16.53417	3.48570	-0.04805
49-98	17.94120	0.42835	-0.03586
49-99	17.92299	-5.66182	0.02745

Table S3. The electronic couplings for all the hopping pathways of **Hept-CO**

Pathway	center-center/Å	V_h/meV	V_e/meV
17-1	16.84221	0.00963	-0.45449
17-3	15.45878	0.00780	0.02369
17-6	16.58695	0.02024	0.17297

17-7	10.17935	0.29044	0.78468
17-10	17.01898	-3.59167	-0.88859
17-13	9.46209	4.28320	2.55473
17-16	19.00192	0.23908	-0.22320
17-19	5.62160	51.62460	96.54010
17-20	17.34167	0.14136	-0.04044
17-23	8.67819	-22.30476	-51.13719

Reference

(1) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112-122

(2) E. F. Valeev, V. Coropceanu, D. A. da Silva Filho, S. Salman, J.-L. Brédas, *J. Am. Chem. Soc*. 2006, **128**, 9882-9886;

(3) A. Troisi, G. Orlandi, *J. Phys. Chem. B*, 2002, **106**, 2093-2101.