Supporting information for

Approaching a Stable, Green Twisted Heteroacene Through "Clean reaction" Strategy

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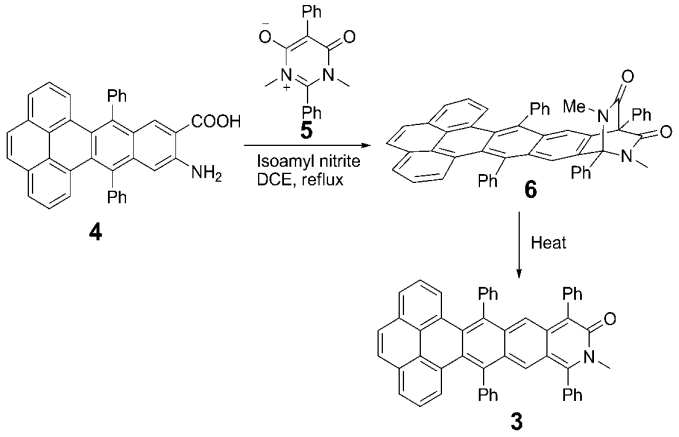
Contents

1. General methods

1.1 Measurements. The NMR spectra were taken on a Bruker ARX 400 and 500 spectrometer. Electrochemistry was carried out with a BAS 100B/W potentiostat, employing a platinum button (diameter: 1.6 mm; area 0.02 cm^2), a platinum wire and a 0.01 M $Ag/AgNO_3$ (Ag/Ag^+) as working, counter and reference electrode, respectively. 0.1 M of tetrabutylammonium perchlorate (TBAP) in ODCB was used as the electrolyte. Since compound **3** was not very soluble in ODCB at room temperature, CV measurements were conducted at higher temperatures (*ca.* 150 °C).

Single-crystal data set of precursor **6** was collected at 103 K on a Bruker SMART APEX II CCD fitted with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Data processing (APEXII and SMART) and absorption correction (SADABS) were accomplished by standard methods. The structure was solved by direct-methods using SHELXS-97 and refinement (anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.376P]$ for $P = (F_o^2 + 2F_c^2)/3)$ was on F^2 by means of SHELXL-97. CCDC number for compound **6** is 858853.

Materials. Meso-ionic pyrimidines (**5**)[1] and 3-amino-5,12-diphenyl-6:7,10:11-bisbenzotetracene-2-carboxylic acid (**4**)[2] were prepared from reported procedures. All solvents were used without further purification.



2. Synthesis

2.1 Lactam cycloadduct 6. To mesoion **5** (114 mg, 0.39 mmol) and isoamyl nitrite (0.060 mL, 0.40 mmol) in 20 mL DCE was added a suspension of 3-amino-5,12-diphenyl-6:7,10:11-

bisbenzotetracene-2-carboxylic acid (**4**) (100 mg, 0.20 mmol) in 10 mL DCE over a span of 1h. After refluxing for an additional hour, DCE was removed. The resulting brown residue was purified by silica-gel column chromatography using dichloromethane : diethyl ether (9:1) as eluent to yield the lactam **6** (88 mg, 60%) as a tan powder; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.12 (d, 2H), 8.05 (s, 1H), 7.88-7.85 (m, 6H), 7.79 (bs, 2H), 7.54-7.24 (bm, 19H), 2.71 (d, 6H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 171.90, 142.13, 141.21, 137.06, 136.81, 135.86, 134.73, 131.92, 131.72, 131.62, 131.42, 131.10, 130.81, 130.55, 130.22, 130.1, 130.01, 129.93, 129.82, 129.26, 129.07, 128.80, 128.60, 127.68, 127.61, 127.46, 126.96, 126.86, 126.13, 125.86, 125.78, 125.28, 124.79, 124.73, 119.99, 81.06, 65.99, 33.93; IR (DRIFT) 3053, 2921, 1715, 1675, 1490, 1367, 1206, 1072, 831, 751, 694, 544 cm^{-1}. MS (ESI): 745.01 (M^+ + H), calcd 745.28 (M^+ + H); Elemental analysis, found C, 86.86; H, 4.95; N, 3.55; calcd C, 87.07; H, 4.87; N, 3.76.

2.2 *2*-Methyl-1,4,6,13- tetraphenyl-7:8,11:12-bisbenzo-anthro[g] isoquinolin-3(2*H*)-one 3.

A neat sample of the lactam cycloadduct **6** (117 mg, 0.16 mmol) was purged 3x using nitrogen gas before heating at 220 ^{o}C under vacuum for 4h to give a green powder as **3** (105 mg, 100%). An alternate method is as follows: the lactam cycloadduct **6** was dispersed in tetrahydronaphthalene solvent. The solution was heated up to 220 ^{0}C for 4 hours and slow cooled to room temperature will give dark green crystals (98%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.81-7.44 (m, 11H), 7.44-7.21 (m, 18H), 3.81 (s, 3H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 158.24, 153.97, 141.18, 141.10, 136.82, 135.76, 135.65, 133.26, 132.17, 131.92, 131.78, 131.01, 130.79, 130.72, 130.43, 130.37, 130.17, 129.72, 129.60, 129.22, 129.07, 128.83, 128.76, 128.14, 127.48, 127.31, 126.80, 126.71, 126.19, 125.06, 125.00, 119.99, 117.40, 115.82, 37.18; IR (DRIFT): 3053, 2923, 1703, 1630, 1447, 1382, 1350, 1012, 829, 750, 701; MS (ESI): 688.47 (M^+ + H), calcd 688.26 (M^+ + H); MS (HiResMAlDI-TOF): 688.2637 (M^+ + H), calcd 688.2640 (M^+ + H), Elemental analysis, found C, 90.56; H, 4.65; N, 2.11; calcd C, 90.80; H, 4.84; N, 2.04.

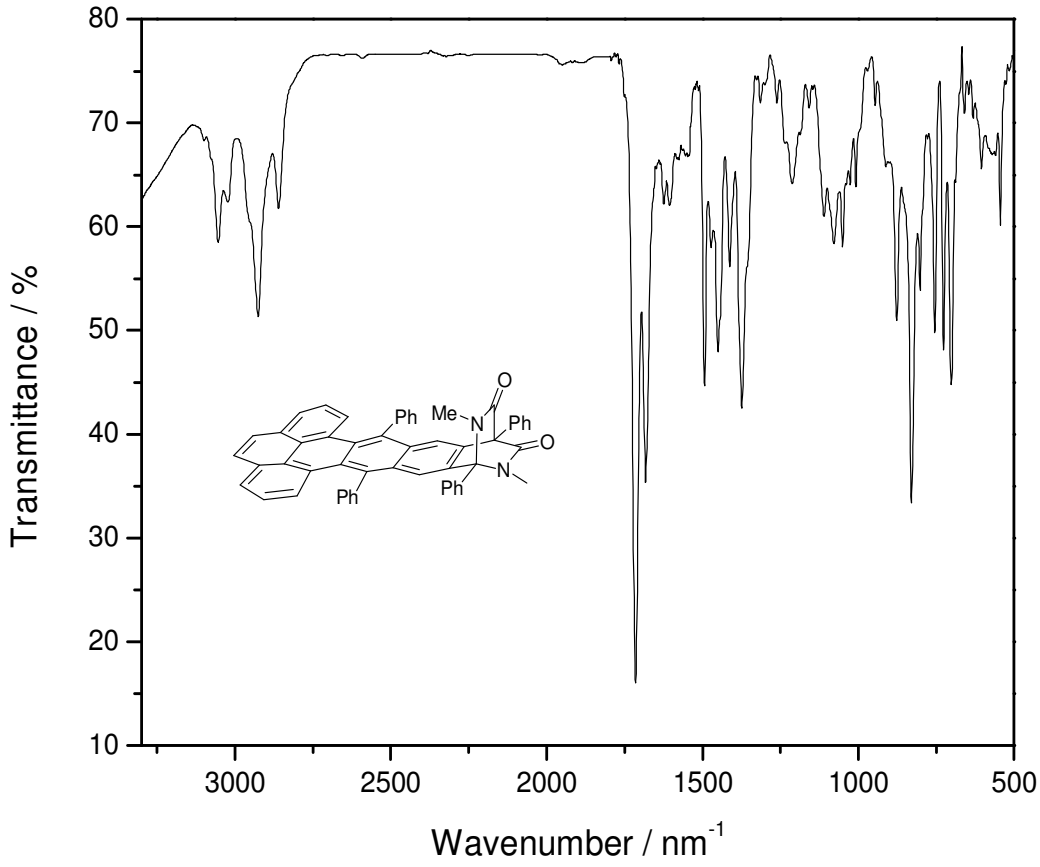


Figure S1. The IR spectrum of compound **6**.

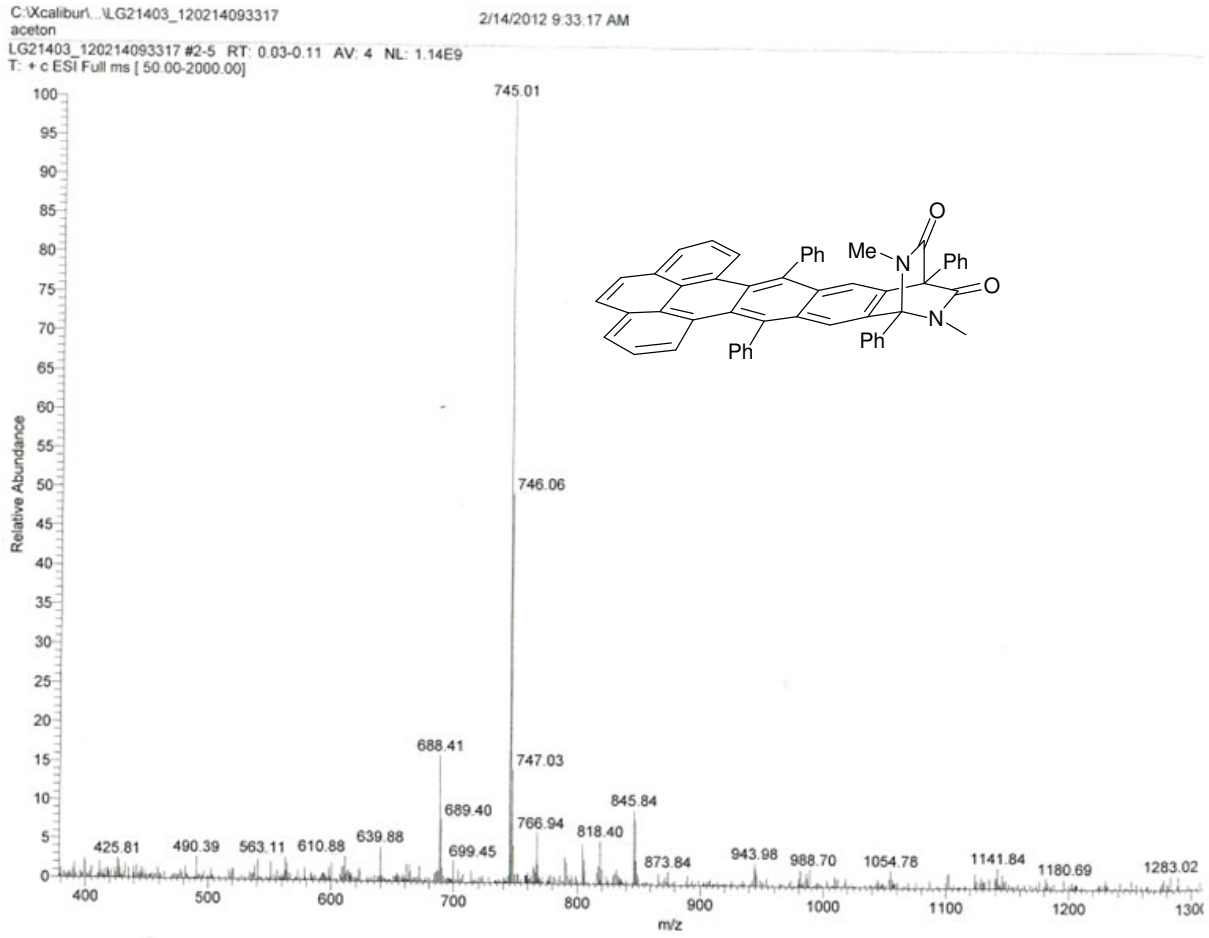


Figure S2. The MS (ESI) spectrum of compound **6**.

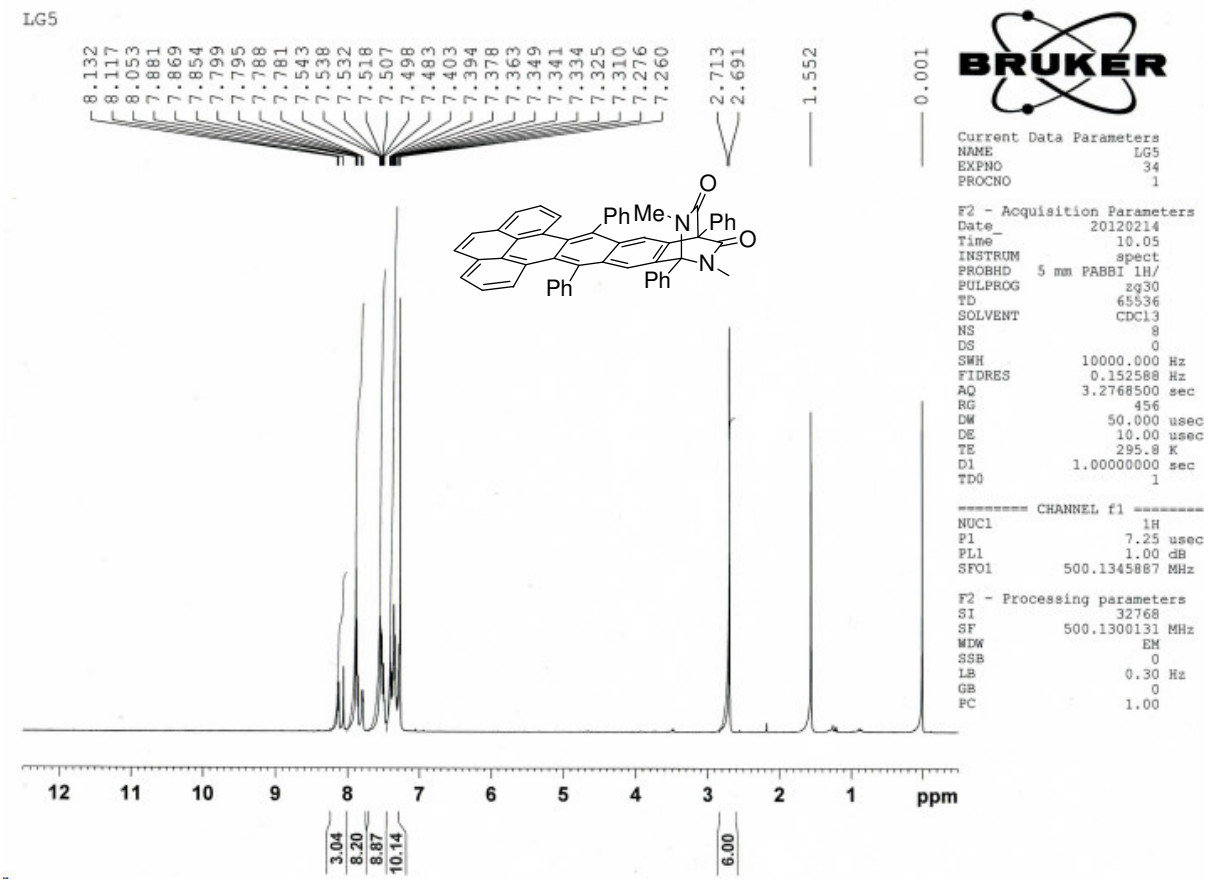


Figure S3. The ^{1}H-NMR spectrum of compound **6**.

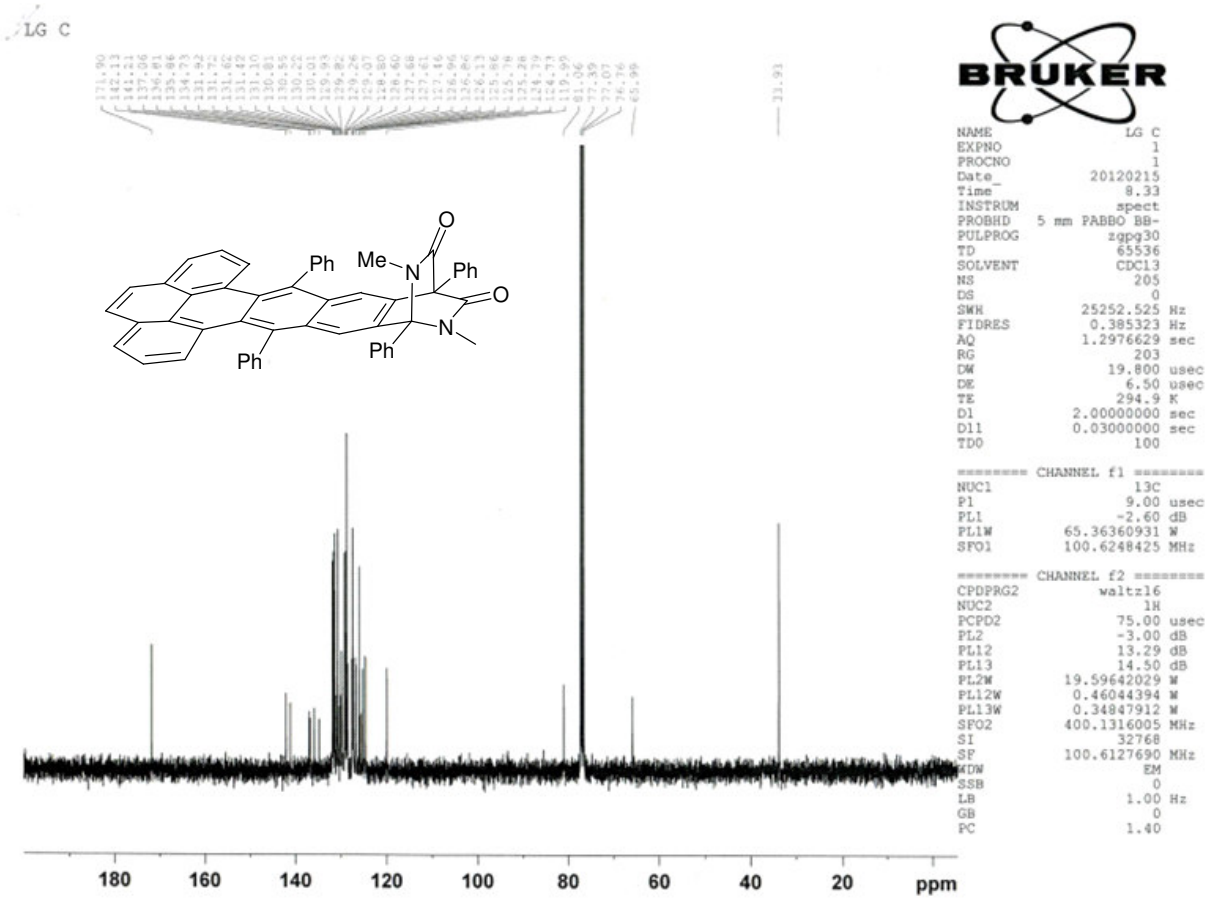
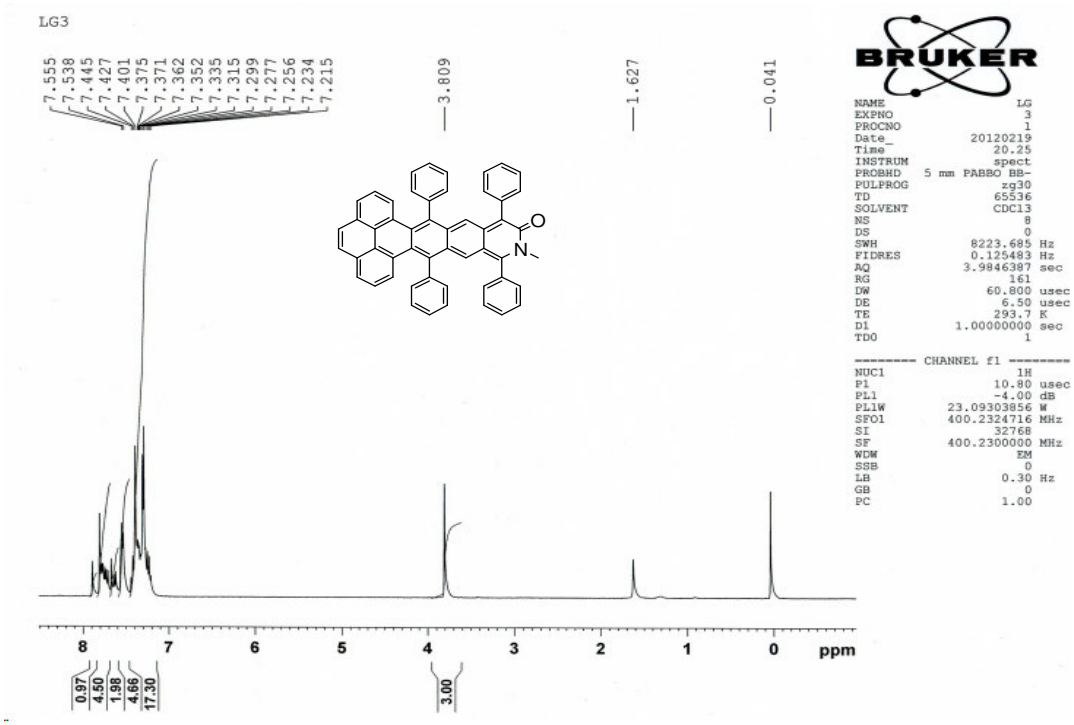
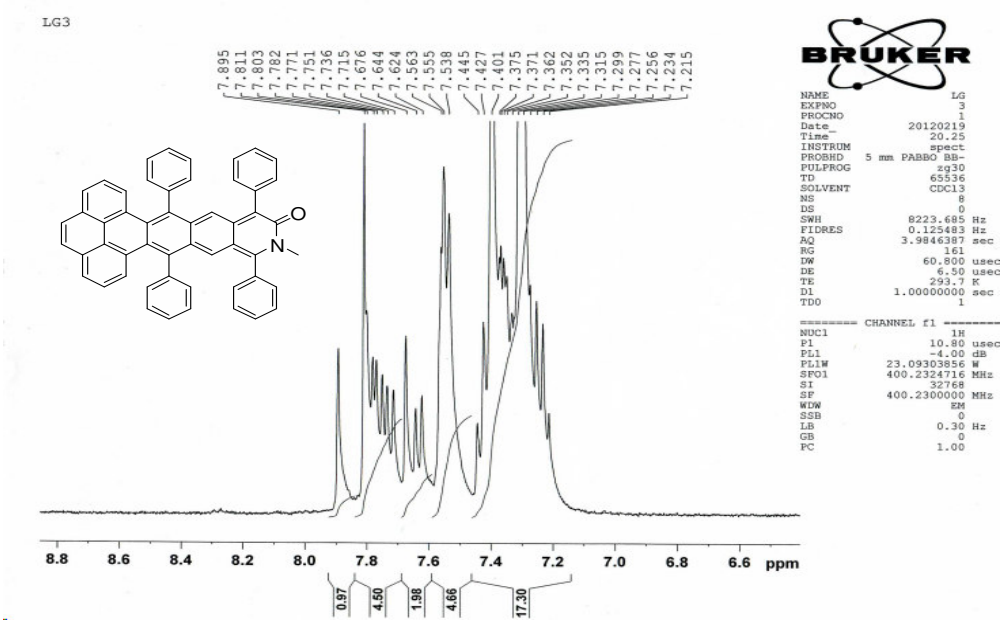


Figure S4. The ^{13}C-NMR spectrum of compound **6**.



(a)



(b)

Figure S5. (a) The ^{1}H-NMR spectrum of compound **3**. (b) The magnified part of ^{1}H-NMR spectrum.

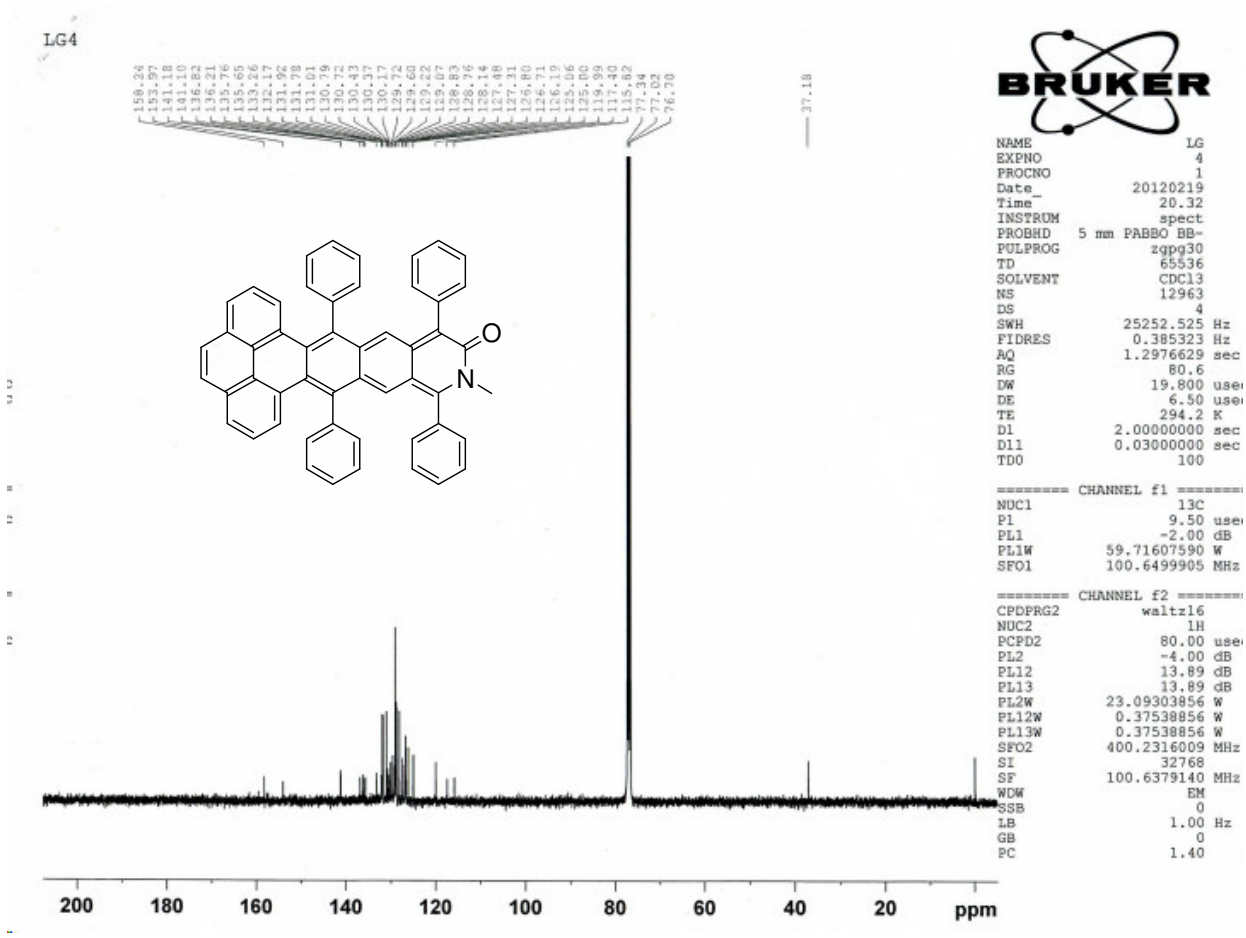


Figure S6. The ^{13}C-NMR spectrum of compound **3**.

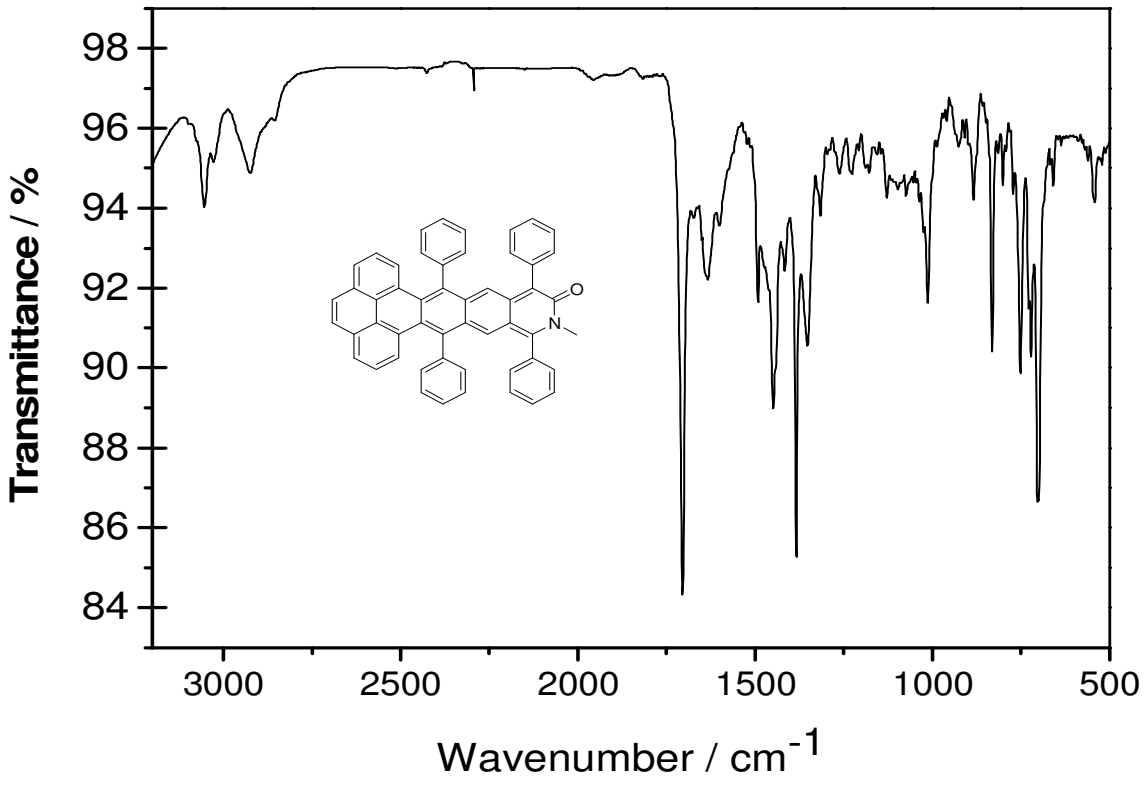


Figure S7. The FT-IR spectrum of compound **3**.

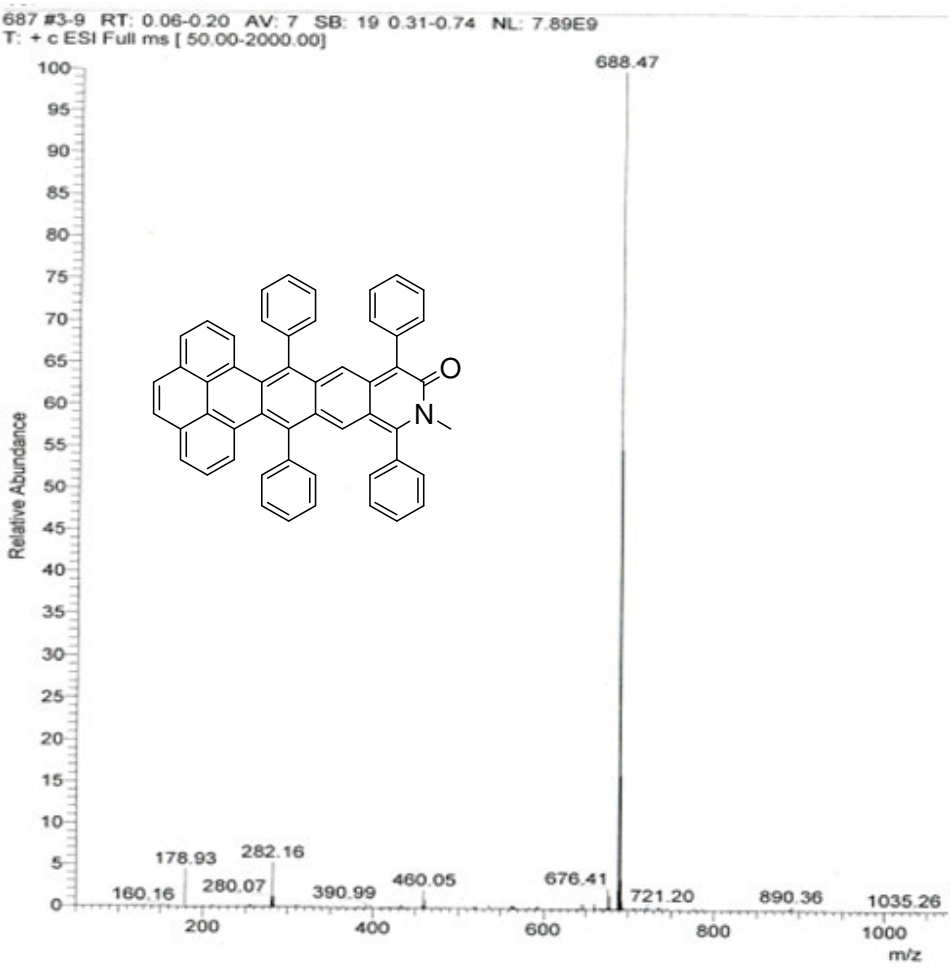


Figure S8. The MS-ESI spectrum of compound **3**.

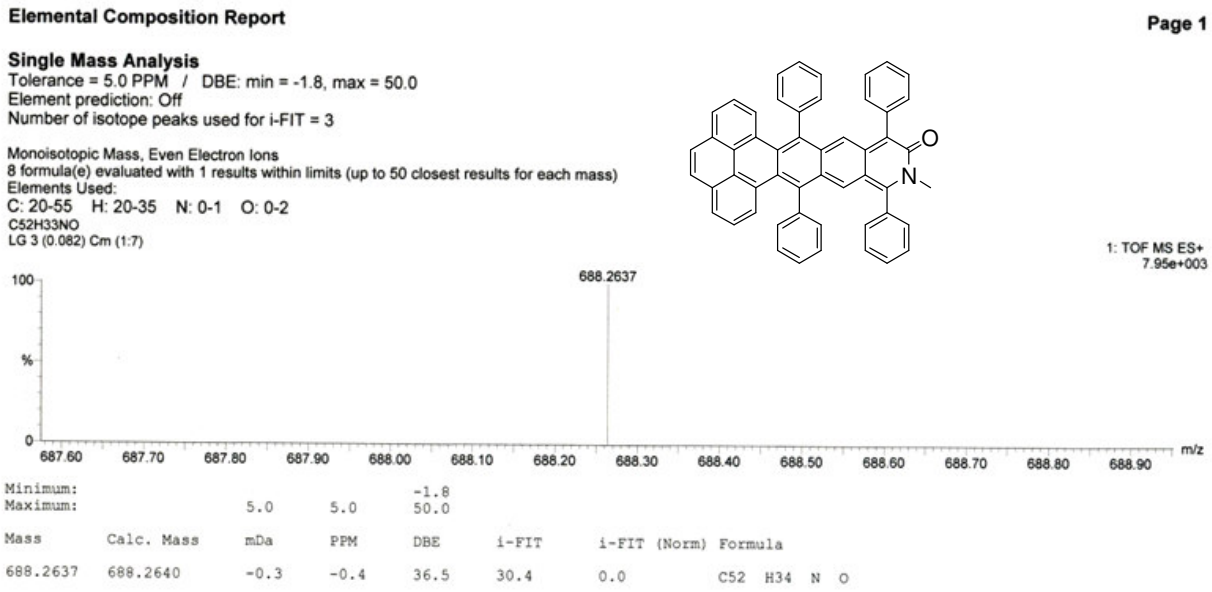


Figure S9. The MS-HiResMAlDI-TOF plot of compound **3**.

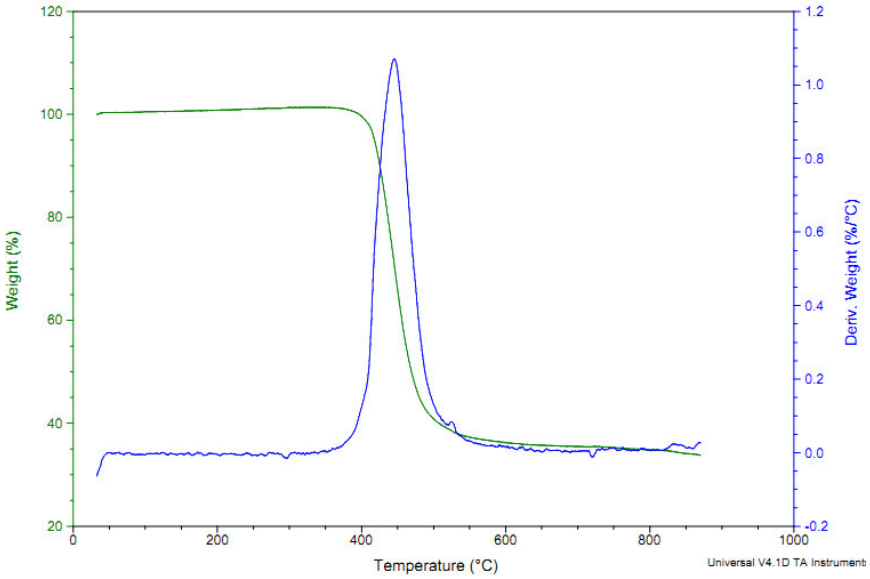


Figure S10. The TGA analysis of compound **3**.

3. X-ray crystallographic data of compound 6

Table S1. Cell data parameters of Compound **6**

Empirical formula	C55 H37Cl3 N2 O2
Color and Habit	colorless plate
Crystal Size (mm)	0.20×0.18×0.06
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	10.887(4)
b (Å)	11.448(4)
c (Å)	17.595(6)
alpha (deg.)	102.152(5)
beta (deg.)	96.560(5)
gamma (deg.)	104.691(5)
Volume($Å^3$)	2041.0(11)
Z	2
Formula weight	864.22
Density(cal.)(g/cm^3)	1.406
Absorption coefficient(mm^{-1})	0.274
F(000)	896
Radiation	MoK\a 0.71073A
Temperature(K)	100(2)
Theta range (deg.)	1.90 to 28.29
Reflections measured	18317
Index ranges of measured data	-14<=h<=14, -14<=k<=15, -22<=l<=22
Independent reflections	9525 (R_{int} = 0.0403)
Observed Reflection	6235 (>2sigma(I))
Final R indices (obs.)	R1 = 0.0484, wR2 = 0.1068
R indices (all)	R1 = 0.0902, wR2 = 0.1323
Goodness-of-fit	0.769

Table S2. Bond lengths (Å) and angles (deg.).

O(1)-C(30)	1.214(3)	C(22)-C(39)	1.424(3)
O(2)-C(38)	1.222(3)	C(22)-C(23)	1.547(3)
N(1)-C(30)	1.378(3)	C(23)-C(24)	1.527(3)
N(1)-C(53)	1.473(3)	C(23)-C(38)	1.548(3)
N(1)-C(31)	1.498(3)	C(23)-C(30)	1.570(3)
N(2)-C(38)	1.356(3)	C(24)-C(29)	1.394(4)
N(2)-C(54)	1.467(3)	C(24)-C(25)	1.399(4)
N(2)-C(31)	1.483(3)	C(25)-C(26)	1.391(4)
C(1)-C(2)	1.394(3)	C(26)-C(27)	1.382(4)
C(1)-C(50)	1.395(3)	C(27)-C(28)	1.386(4)
C(2)-C(3)	1.376(4)	C(28)-C(29)	1.392(4)
C(3)-C(4)	1.395(4)	C(31)-C(32)	1.519(3)
C(4)-C(51)	1.424(3)	C(31)-C(39)	1.531(3)
C(4)-C(5)	1.442(4)	C(32)-C(33)	1.393(4)
C(5)-C(6)	1.346(4)	C(32)-C(37)	1.398(4)
C(6)-C(7)	1.434(4)	C(33)-C(34)	1.389(4)
C(7)-C(8)	1.401(4)	C(34)-C(35)	1.387(4)
C(7)-C(52)	1.433(3)	C(35)-C(36)	1.384(4)
C(8)-C(9)	1.374(4)	C(36)-C(37)	1.384(4)
C(9)-C(10)	1.398(4)	C(39)-C(40)	1.354(3)
C(10)-C(11)	1.394(3)	C(40)-C(41)	1.430(3)
C(11)-C(52)	1.419(3)	C(41)-C(42)	1.423(3)
C(11)-C(12)	1.490(3)	C(42)-C(49)	1.409(3)
C(12)-C(13)	1.402(3)	C(42)-C(43)	1.495(3)
C(12)-C(49)	1.443(3)	C(43)-C(48)	1.386(3)
C(13)-C(20)	1.422(3)	C(43)-C(44)	1.397(3)
C(13)-C(14)	1.497(3)	C(44)-C(45)	1.388(4)
C(14)-C(15)	1.389(4)	C(45)-C(46)	1.384(4)
C(14)-C(19)	1.399(3)	C(46)-C(47)	1.387(4)
C(15)-C(16)	1.394(4)	C(47)-C(48)	1.392(4)
C(16)-C(17)	1.387(4)	C(49)-C(50)	1.487(3)
C(17)-C(18)	1.379(4)	C(50)-C(51)	1.427(3)
C(18)-C(19)	1.382(4)	C(51)-C(52)	1.431(3)
C(20)-C(41)	1.413(3)	C(1S)-Cl(3)	1.758(3)
C(20)-C(21)	1.432(3)	C(1S)-Cl(1)	1.756(3)
C(21)-C(22)	1.368(3)	C(1S)-Cl(2)	1.767(3)
C(30)-N(1)-C(53)	114.2(2)	C(27)-C(28)-C(29)	121.0(3)
C(30)-N(1)-C(31)	113.8(2)	C(28)-C(29)-C(24)	120.5(3)
C(53)-N(1)-C(31)	119.0(2)	O(1)-C(30)-N(1)	123.4(2)
C(38)-N(2)-C(54)	119.0(2)	O(1)-C(30)-C(23)	122.9(2)
C(38)-N(2)-C(31)	117.2(2)	N(1)-C(30)-C(23)	113.5(2)
C(54)-N(2)-C(31)	122.6(2)	N(2)-C(31)-N(1)	106.83(19)
C(2)-C(1)-C(50)	122.3(2)	N(2)-C(31)-C(32)	108.8(2)
C(3)-C(2)-C(1)	120.5(2)	N(1)-C(31)-C(32)	113.4(2)

C(2)-C(3)-C(4)	119.9(2)	N(2)-C(31)-C(39)	107.2(2)
C(3)-C(4)-C(51)	120.0(2)	N(1)-C(31)-C(39)	103.44(19)
C(3)-C(4)-C(5)	120.5(2)	C(32)-C(31)-C(39)	116.6(2)
C(51)-C(4)-C(5)	119.5(2)	C(33)-C(32)-C(37)	118.3(2)
C(6)-C(5)-C(4)	121.3(2)	C(33)-C(32)-C(31)	122.0(2)
C(5)-C(6)-C(7)	121.2(2)	C(37)-C(32)-C(31)	119.4(2)
C(8)-C(7)-C(52)	119.9(2)	C(34)-C(33)-C(32)	120.4(3)
C(8)-C(7)-C(6)	121.0(2)	C(35)-C(34)-C(33)	120.3(3)
C(52)-C(7)-C(6)	119.0(2)	C(36)-C(35)-C(34)	119.7(3)
C(9)-C(8)-C(7)	120.0(2)	C(35)-C(36)-C(37)	119.9(3)
C(8)-C(9)-C(10)	120.4(2)	C(36)-C(37)-C(32)	121.1(3)
C(11)-C(10)-C(9)	121.8(2)	O(2)-C(38)-N(2)	123.1(2)
C(10)-C(11)-C(52)	118.1(2)	O(2)-C(38)-C(23)	125.3(2)
C(10)-C(11)-C(12)	122.6(2)	N(2)-C(38)-C(23)	111.6(2)
C(52)-C(11)-C(12)	119.2(2)	C(40)-C(39)-C(22)	120.5(2)
C(13)-C(12)-C(49)	119.6(2)	C(40)-C(39)-C(31)	127.5(2)
C(13)-C(12)-C(11)	121.9(2)	C(22)-C(39)-C(31)	111.6(2)
C(49)-C(12)-C(11)	118.5(2)	C(39)-C(40)-C(41)	121.0(2)
C(12)-C(13)-C(20)	120.3(2)	C(20)-C(41)-C(42)	120.3(2)
C(12)-C(13)-C(14)	122.1(2)	C(20)-C(41)-C(40)	118.8(2)
C(20)-C(13)-C(14)	117.5(2)	C(42)-C(41)-C(40)	120.8(2)
C(15)-C(14)-C(19)	119.1(2)	C(49)-C(42)-C(41)	120.1(2)
C(15)-C(14)-C(13)	118.8(2)	C(49)-C(42)-C(43)	124.8(2)
C(19)-C(14)-C(13)	122.2(2)	C(41)-C(42)-C(43)	115.1(2)
C(14)-C(15)-C(16)	120.5(3)	C(48)-C(43)-C(44)	118.6(2)
C(17)-C(16)-C(15)	119.7(3)	C(48)-C(43)-C(42)	120.9(2)
C(18)-C(17)-C(16)	120.1(3)	C(44)-C(43)-C(42)	120.4(2)
C(19)-C(18)-C(17)	120.5(3)	C(45)-C(44)-C(43)	121.1(2)
C(18)-C(19)-C(14)	120.2(3)	C(46)-C(45)-C(44)	119.6(3)
C(41)-C(20)-C(13)	119.0(2)	C(45)-C(46)-C(47)	120.0(2)
C(41)-C(20)-C(21)	118.8(2)	C(46)-C(47)-C(48)	120.2(3)
C(13)-C(20)-C(21)	122.2(2)	C(43)-C(48)-C(47)	120.5(3)
C(22)-C(21)-C(20)	120.9(2)	C(42)-C(49)-C(12)	118.5(2)
C(21)-C(22)-C(39)	119.9(2)	C(42)-C(49)-C(50)	123.3(2)
C(21)-C(22)-C(23)	126.2(2)	C(12)-C(49)-C(50)	118.2(2)
C(39)-C(22)-C(23)	113.6(2)	C(1)-C(50)-C(51)	117.2(2)
C(24)-C(23)-C(22)	113.6(2)	C(1)-C(50)-C(49)	123.3(2)
C(24)-C(23)-C(38)	117.5(2)	C(51)-C(50)-C(49)	119.4(2)
C(22)-C(23)-C(38)	107.21(19)	C(4)-C(51)-C(50)	120.1(2)
C(24)-C(23)-C(30)	111.4(2)	C(4)-C(51)-C(52)	119.0(2)
C(22)-C(23)-C(30)	100.95(19)	C(50)-C(51)-C(52)	120.9(2)
C(38)-C(23)-C(30)	104.55(19)	C(11)-C(52)-C(7)	119.3(2)
C(29)-C(24)-C(25)	117.8(2)	C(11)-C(52)-C(51)	120.8(2)
C(29)-C(24)-C(23)	124.1(2)	C(7)-C(52)-C(51)	119.9(2)
C(25)-C(24)-C(23)	118.1(2)	Cl(3)-C(1S)-Cl(1)	110.21(15)

C(26)-C(25)-C(24)	121.6(2)	Cl(3)-C(1S)-Cl(2)	110.11(15)
C(27)-C(26)-C(25)	120.0(3)	Cl(1)-C(1S)-Cl(2)	111.30(15)
C(26)-C(27)-C(28)	119.2(3)		

4. References

1. Kappe, T.; Pocivalnik, D. *Heterocycles* **1983**, *20*, 1367.

2. Zhang, Q.; Divayana, Y.; Xiao, J.; Wang, Z.; Tiekink, E. R. T.; Doung, H. M.; Zhang, H.; Boey, F.; Sun, X. W.; Wudl F. *Chem. Eur. J.* **2010**, *16*, 7422**..**