Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

for

A Bowl-Shaped Molecule for Organic Field-Effect Transistors: Crystal Engineering and Charge Transport Switching by Oxygen Doping

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1. Experimental Section

General. Chemical reagents and PS were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium prior to use. 1,8-Diazabicycloundec-7-ene (DBU) and N,N-dimethylformamide (DMF) were distilled under reduced pressure. Column chromatography was performed with silica gel. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica gel coated glass sheets with F254 indicator. All yields given refer to isolated yields. Nuclear Magnetic Resonance (NMR) spectra were recorded on 400 MHz or 500 MHz Bruker AVANCE III spectrometers. Chemical shifts are reported in ppm. Coupling constants (*J* values) are reported in Hertz. ^{1}H NMR chemical shifts were referenced to TMS (0 ppm). ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.00 ppm). ESI-HRMS spectra were recorded on a Bruker Apex IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Elemental analyses were carried out on a German Vario EL III elemental analyzer.

Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis Spectrometer. Photoluminescence spectra were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer with a right-angle geometry. Cyclic voltammetry was performed on BASI Epsilon workstation and measurements were carried out in dichloromethane containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte (scan rate: 50 mV s^{-1}). Glassy carbon electrode was used as a working electrode, a platinum sheet as a counter electrode and Ag/AgCl as a reference electrode. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q600 analyzer under N_2 (10 ℃ min^{-1}). Differential scanning calorimetry (DSC) was performed on a METTLER TOLEDO Instrument DSC822e calorimeter under N_2.

Synthetic Procedures.

Compounds 1. A solution of 2-chlorobenzeneacetic acid (1.7 g, 10 mmol) in dry dichloromethane was added slowly to a solution of DCC (1.44 g, 7 mmol) and DMAP (366 mg, 3 mmol) in dry dichloromethane. The reaction mixture was kept for 12 h at room temperature and then filtered. The filtrate was distilled off and the residue was purified by silica gel chromatography with eluent (PE: EtOAc = 20:1) to give **1** as a white solid (1.17 g, 4.2 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37-7.41 (m, 2H), 7.21-7.24 (m, 6H), 3.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 203.1, 134.5, 132.6, 131.8, 129.6, 128.7, 127.0, 47.2. ESI-HRMS calcd. for $[C_{15}H_{12}Cl_2O + H]^+$: 279.0346; Found: 279.0338.

Compound 2. Ethanolic KOH (56 mg, 1 mmol) was added dropwise to a suspension of **1** (307 mg, 1.1 mmol) and acenaphthoquinone (182 mg, 1 mmol) in 10 mL of boiling ethanol. The suspension was refluxed for 15 min, and then cooled in an ice bath. The solid was separated by filtration. The residue was washed with cold ethanol until the filtrate was colorless, and then dried under reduced pressure. The product was used in the subsequent Diels-Alder reaction without further purification.

Compound 3. A mixture of **2** (850 mg, 2 mmol) and 1-octyl-pyrrole-2,5-dione (1.25 g, 6 mmol) in nitrobenzene was refluxed for 12 h. Nitrobenzene was removed by distillation under reduced pressure. The residue was purified by column chromatography (silica gel) with eluent (PE: EtOAc =40:1) to give **3** as a yellow solid (907 mg, 1.5 mmol, 73% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.87-7.89 (d, *J* = 8.0 Hz, 2H), 7.69-7.71 (d, *J* = 7.6 Hz, 2H), 7.56-7.61 (m, 2H), 7.52-7.55 (m, 4H), 7.41-7.45 (m, 2H), 6.88-6.89 (d, *J* = 7.2 Hz, 2H), 3.52-3.56 (t, *J* = 7.6 Hz, 2H), 1.60-1.63 (m, 2H), 1.22-1.25 (m, 10H), 0.83-0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 167.4, 142.9, 134.6, 134.4, 133.5, 133.2, 132.0, 130.4, 130.2, 130.0, 129.7, 128.7, 128.3, 127.2, 124.7, 38.1, 31.7, 29.1, 29.1, 28.5, 27.0, 22.6, 14.0. ESI-HRMS calcd. for $[C_{38}H_{31}Cl_2NO_2 + H]^+$: 604.1818; Found: 604.1805.

Compound CI-1. A solution of **3** (121 mg, 0.2 mmol), $Pd(PCy_3)_2Cl_2$ (60 mg, 0.04 mmol) and DBU (180 mg, 1.2 mmol) in DMF (10 mL) was heated at 160 ℃ for 36 h. The reaction mixture was washed with aqueous NaCl and extracted with chloroform and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel with eluent (PE: EtOAc =40:1) to give **CI-1** as a light yellow solid (87 mg, 0.16 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 9.87-9.89 (d, *J* = 7.6 Hz, 2H), 8.06-8.08 (d, *J* = 7.2 Hz, 2H), 7.57-7.65 (m, 4H), 7.50-7.52 (d, *J* = 8.4 Hz, 2H), 7.33-7.35 (d, *J* = 8.4 Hz, 2H), 3.66-3.70 (t, *J* = 7.6 Hz, 2H), 1.73-1.79 (m, 2H), 1.25-1.52 (m, 10H), 0.89-0.93 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 168.0, 134.3, 132.4, 131.7, 131.2, 131.0, 130.6, 130.5, 128.0, 127.7, 127.5, 127.4, 127.2, 123.8, 123.1, 122.1, 38.2, 31.9, 29.4, 29.4, 28.9, 27.3, 22.7, 14.2. ESI-HRMS calcd. for $[C_{38}H_{29}NO_2 + H]^+$: 532.2278; Found: 532.2271.

2. Concentration-dependent ^{1}H NMR Spectra

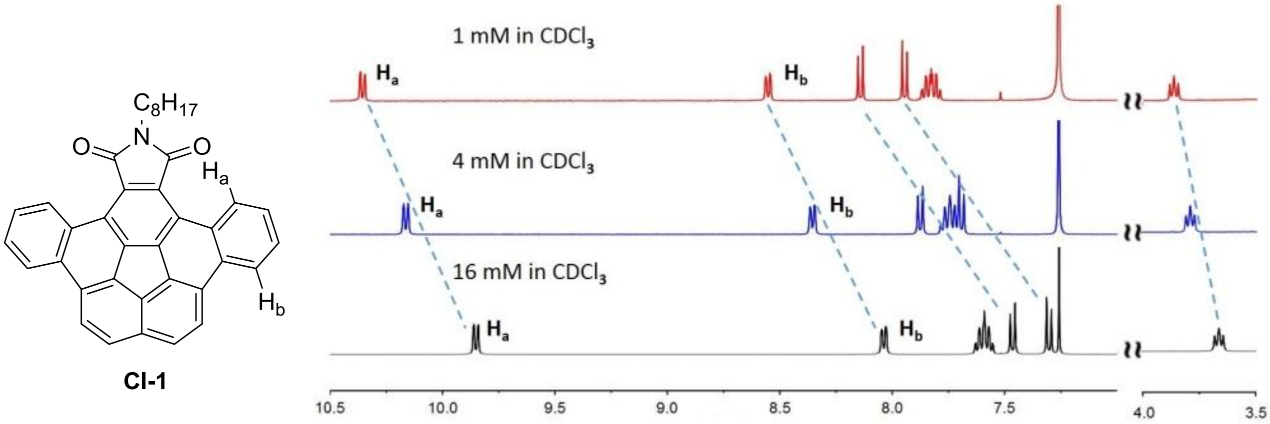


Figure S1. Comparison of ^{1}H NMR spectra of **CI-1** at different concentrations.

Concentration-dependent ^{1}H NMR spectra were performed to investigate the intermolecular π-π interaction of **CI-1**. As shown in Figure S1, when the concentration of **CI-1** is increased from 1 mM to 16 mM, the signal assigned to the proton H_a at a chemical shift of 10.3 ppm shifted upfield to 9.8 ppm. Other signals of aromatic protons exhibited similar upfield shift, which is caused by the shielding from the ring current of neighboring aromatic molecules within a cofacial stacking.[1] These results indicate that the self-assembly behaviors of **CI-1**, which has a buckybowl structure similar to corannulene, could be tuned by the introduction of another molecular dipole caused by the imide group. The resulting convex-concave stacking of the bowl-shaped skeleton is beneficial to the charge transport.

3. Thermal Properties (TGA and DSC)

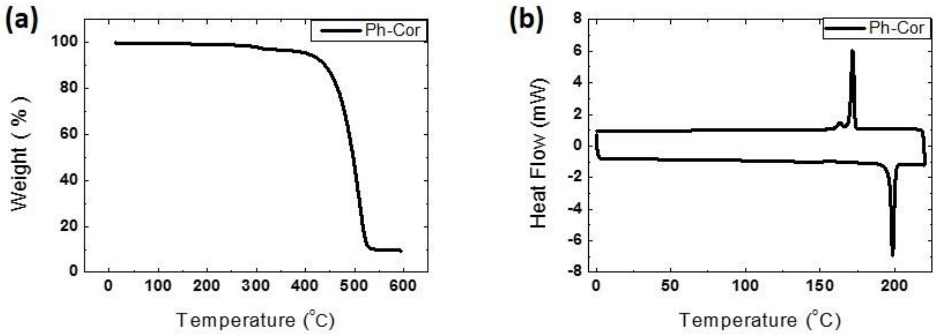


Figure S2. (a) Thermogravimetric analysis (TGA) of **CI-1** (5% weight loss: 406 °C). (b) DSC trace of **CI-1**.

4. Concentration-Dependent Absorption Spectra

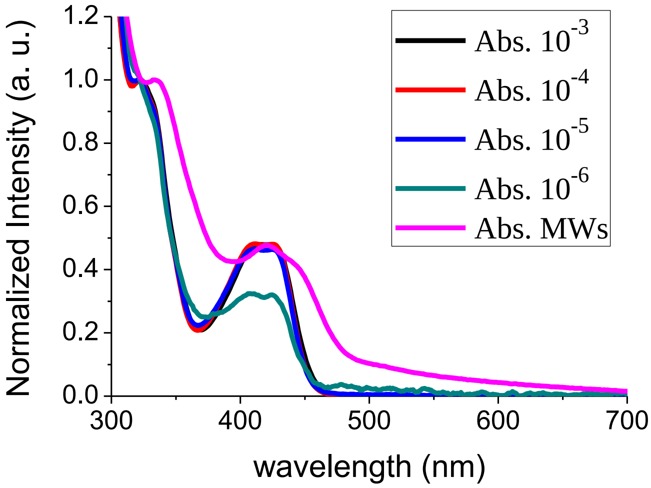


Figure S3. Concentration-dependent absorption spectra of **CI-1** in CH_2Cl_2.

5. Cyclic Voltammograms

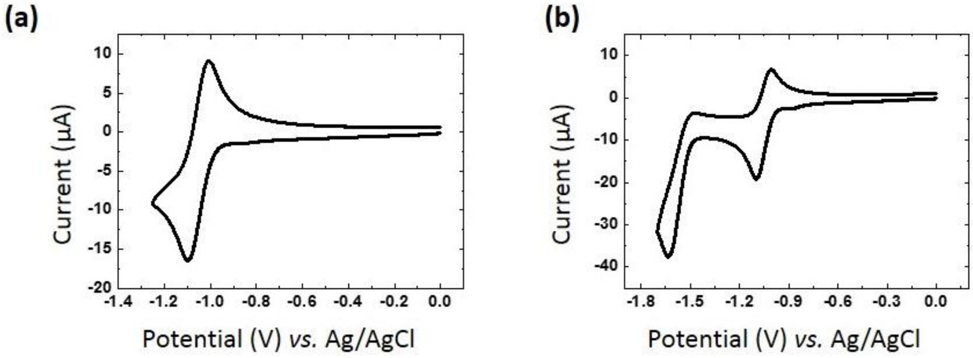


Figure S4. Cyclic voltammogram of **CI-1**. The LUMO energy level is estimated from LUMO = −4.80 – E_{red} to be –3.40 eV. The HOMO energy level is estimated from HOMO = LUMO – E_g^{opt} to be –6.15 eV.

6. Single Crystal Structures

Single crystal suitable for X-ray analysis was obtained from toluene/MeOH.

Table S1. Crystal data and structure refinement for **CI-1**

Empirical formula	$C_{38}H_{29}NO_2$
Formula weight	531.62
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.2711(3)
b/Å	11.9307(5)
c/Å	29.9623(13)
α/°	95.055(3)
β/°	95.380(4)
γ/°	95.045(3)
Volume/$Å^3$	2565.55(19)
Z	4
ρ_{calc}mg/mm^3	1.376
m/mm^{-1}	0.084
F(000)	1120.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
2Θ range for data collection	6.54 to 52.04 °
Index ranges	$-6 \leq h \leq 8$, $-12 \leq k \leq 14$, $-36 \leq l \leq 24$
Reflections collected	14297
Independent reflections	9387[R(int) = 0.0465]
Data/restraints/parameters	9387/0/741
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	$R_1 = 0.0576$, $wR_2 = 0.1292$
Final R indexes [all data]	$R_1 = 0.0838$, $wR_2 = 0.1415$
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.26

7. OFET Fabrication and Characterization

300-nm-thick SiO_2 was thermally deposited on the heavily n-doped Si substrate. The silicon wafers with 300 nm thermally grown SiO_2 were cleaned by sonication in acetone, detergent, deionized water (twice) and *iso*-propanol sequentially and were dried in a vacuum oven at 80 ℃ for 30 min. After treated with oxygen-plasma for 15 min, films of PS were spin-coated onto the SiO_2 substrate at 4000 rpm for 40 s and then were baked at 80 ℃ for 0.5 h in a glovebox. The thickness of the PS layer was measured to be 43 nm. The organic self-assembled microribbon suspensions were spin-coated onto the substrates. The substrates with microribbons were baked in the vacuum oven at 80 ℃ overnight.

The FET characteristics were measured using a Vector BX4000 probe station connected to a Keithley SCS 4200 in air and a LakeShore TTPX probe station connected to a Keithley 2636A semiconductor analyzer under vacuum. The carrier mobility, μ, was calculated from the data in the saturated regime according to the equation $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$, where I_{SD} is the drain current in the saturated regime. W and L are the semiconductor channel width and length, respectively. C_i (C_i = 9.4 nF) is the capacitance per unit area of the gate dielectric layer. V_G and V_T are the gate voltage and threshold voltage, respectively. $V_G - V_T$ of the device was determined from the relationship between the square root of I_{SD} and V_G at the saturated regime.

8. Computational Studies

The geometries of **CI-1** were first optimized at the B3LYP/6-31G(d) level, and the HOMO, LUMO and molecular dipole moment were then calculated with the 6-311+G(d,p) basis set, using the Gaussian 09 software package.[2] The intermolecular electronic couplings were evaluated by the local density functional VWN in conjunction with the PW91 gradient corrections with the double-ζ plus polarization (DZP) basis set using the Amsterdam Density Functional (ADF) program package.[2]

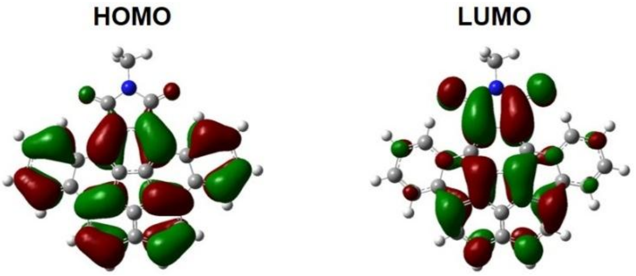


Figure S5. Calculated molecular orbitals of **CI-1**.

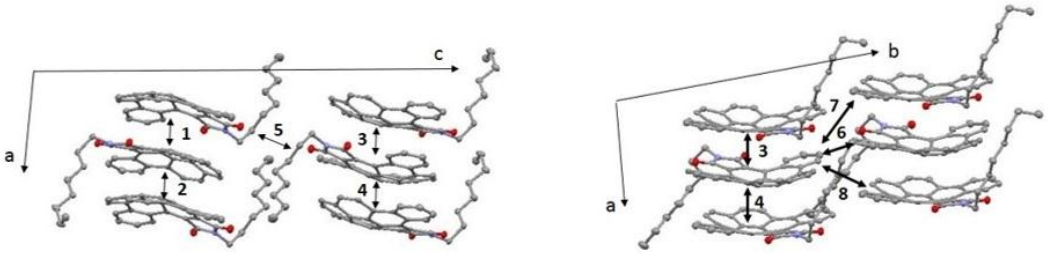


Figure S6. Electronic couplings V (meV) in the single crystal of **CI-1**.

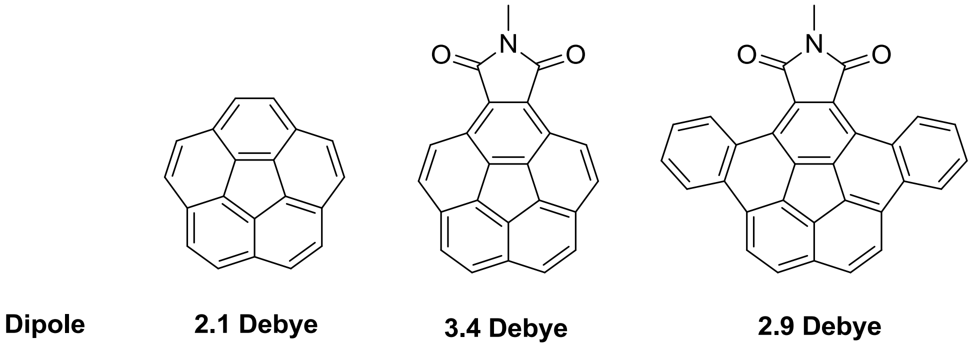


Figure S7. Calculated molecular dipole moment of corannulene, imide-fused corannulene and **CI-1**.

Table S2. Calculation of electronic couplings V in the single crystals of **CI-1**.

Route	J_{RP} (eV)[a]	S_{RP}[b]	H_{RR} (eV)[c]	H_{PP} (eV)[c]	V_{HOMO} (eV)[d]	V_{HOMO} (meV)
1	0.27660	-0.02607	-6.08506	-6.05481	0.118437290	118.4372898
2	0.00526	-0.00113	-6.08730	-6.09734	-0.001624324	-1.624323674
3	0.27644	-0.02606	-6.08479	-6.05476	0.118342032	118.3420324
4	0.00497	-0.00111	-6.09740	-6.08749	-0.001792616	-1.792616159
5	0.00080	-0.00001	-6.35938	-6.35931	0.000736407	0.736406550
6	-0.00837	0.00101	-6.47600	-6.40511	-0.001865041	-1.865041353
7	0.00365	-0.00034	-6.28365	-6.47831	0.001480467	1.480466971
8	0.00085	-0.00010	-6.35191	-6.35018	0.000214896	0.214895502

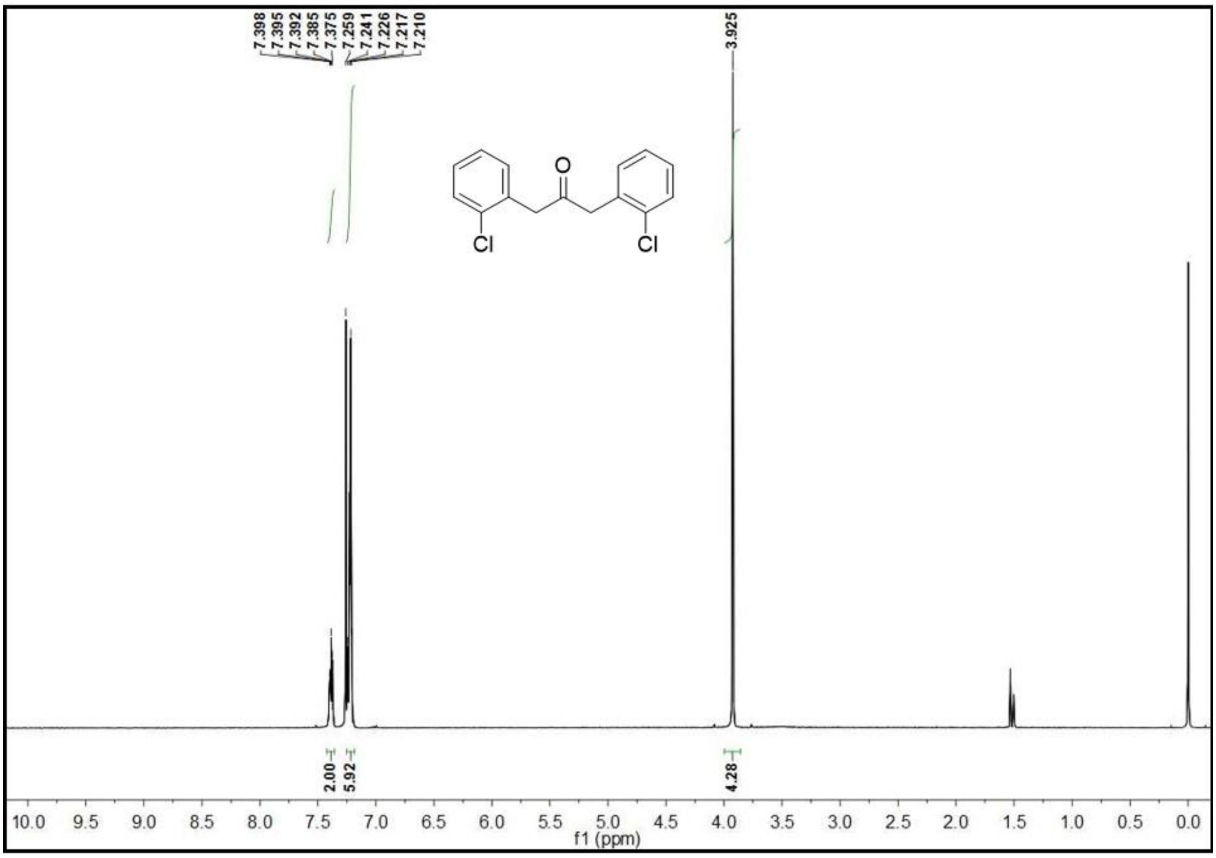
Route	J_{RP} (eV)	S_{RP}	H_{RR} (eV)	H_{PP} (eV)	V_{LUMO} (eV)	V_{LUMO} (meV)
1	-0.04913	0.00554	-3.78133	-3.71773	-0.028358474	-28.35847417
2	-0.14788	0.01653	-3.78103	-3.78919	-0.085335449	-85.33544884
3	-0.04917	0.00554	-3.78073	-3.71776	-0.028400054	-28.40005434
4	-0.14792	0.01653	-3.78931	-3.78055	-0.085378436	-85.37843598
5	0.00012	-0.00003	-4.01803	-4.01797	-0.000000540	-0.000540000
6	0.00095	-0.00013	-4.11097	-4.07820	0.000417704	0.417703957
7	-0.00310	0.00034	-3.95141	-4.14923	-0.001722891	-1.722891399
8	-0.00011	0.00001	-4.00879	-4.00194	-0.000069946	-0.069946350

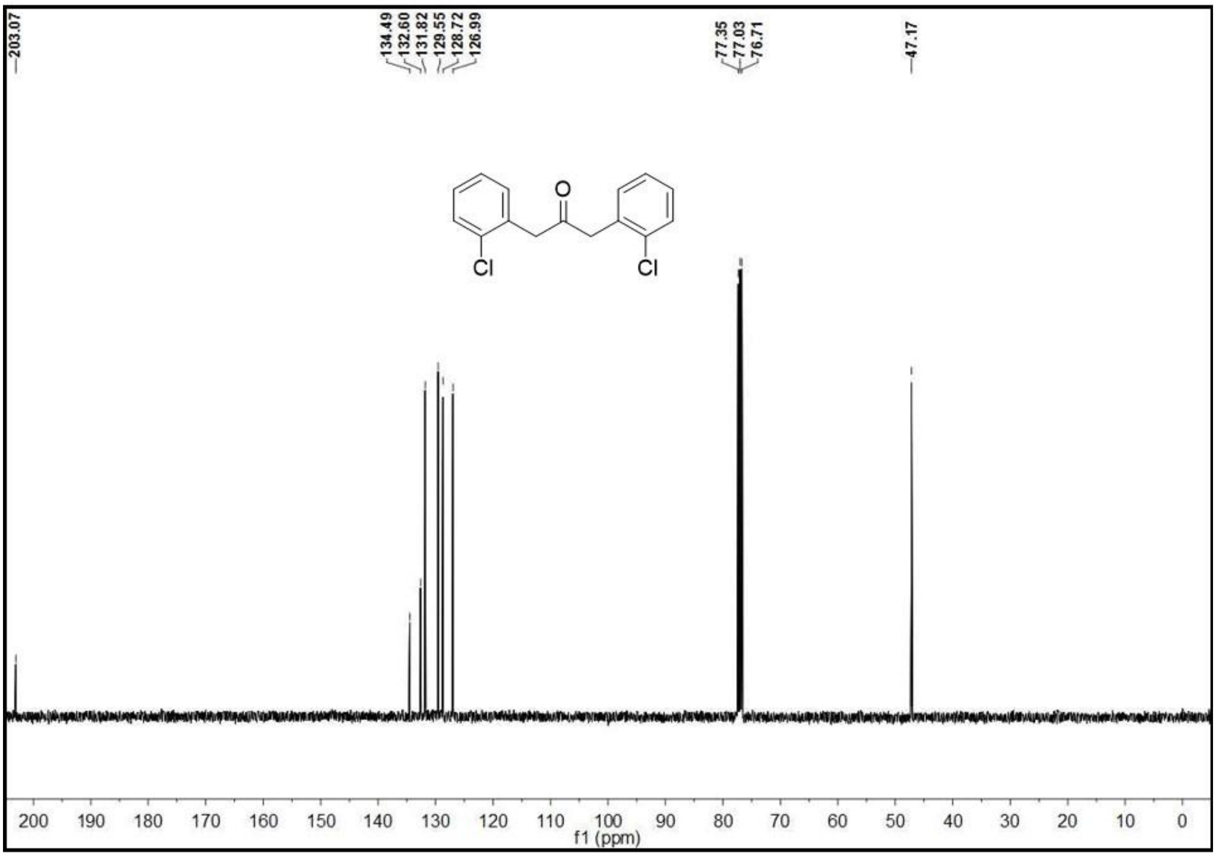
[a] J_{RP}: charge transfer integral; [b] S_{RP}: overlap integral; [c] H_{RR} and H_{PP}: site integral; [d] $V = [J_{RP} - 0.5S_{RP}(H_{RR} + H_{PP})]/(1 - S_{RP}^2)$.

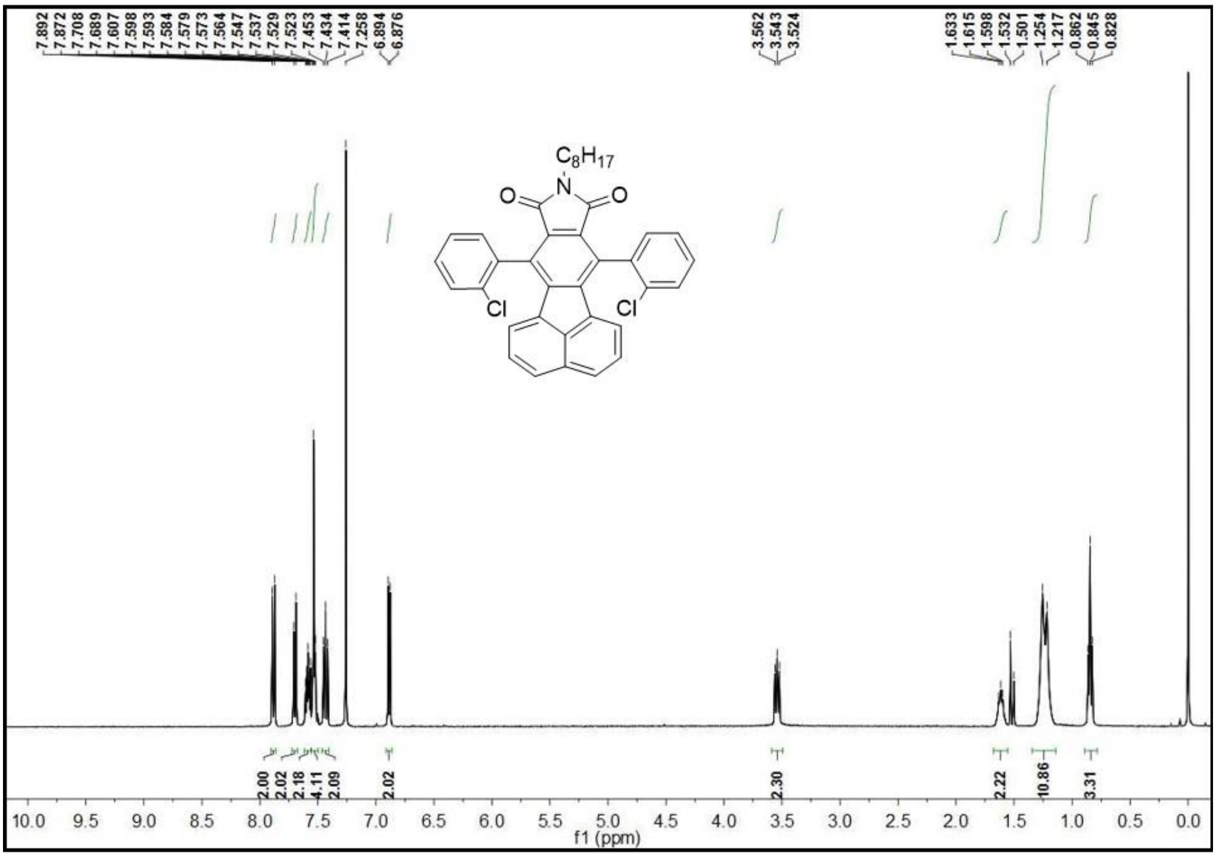
Reference

1. (a) J. Janata, J. Gendell, C.-Y. Ling, W. Barth, L. Backes, J. Mark, H. B., R. G. Lawton, *J. Am. Chem. Soc.*, 1967, **89**, 3056; (b) T. J. Seiders, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.*, 1999, **121**, 7804; (c) C. Bruno, R. Benassi, A. Passalacqua, F. Paolucci, C. Fontanesi, M. Marcaccio, E. A. Jackson, L. T. Scott, *J. Phys. Chem. B*, 2009, **113**, 1954.
2. Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

9. ^{1}H and ^{13}C NMR Spectra



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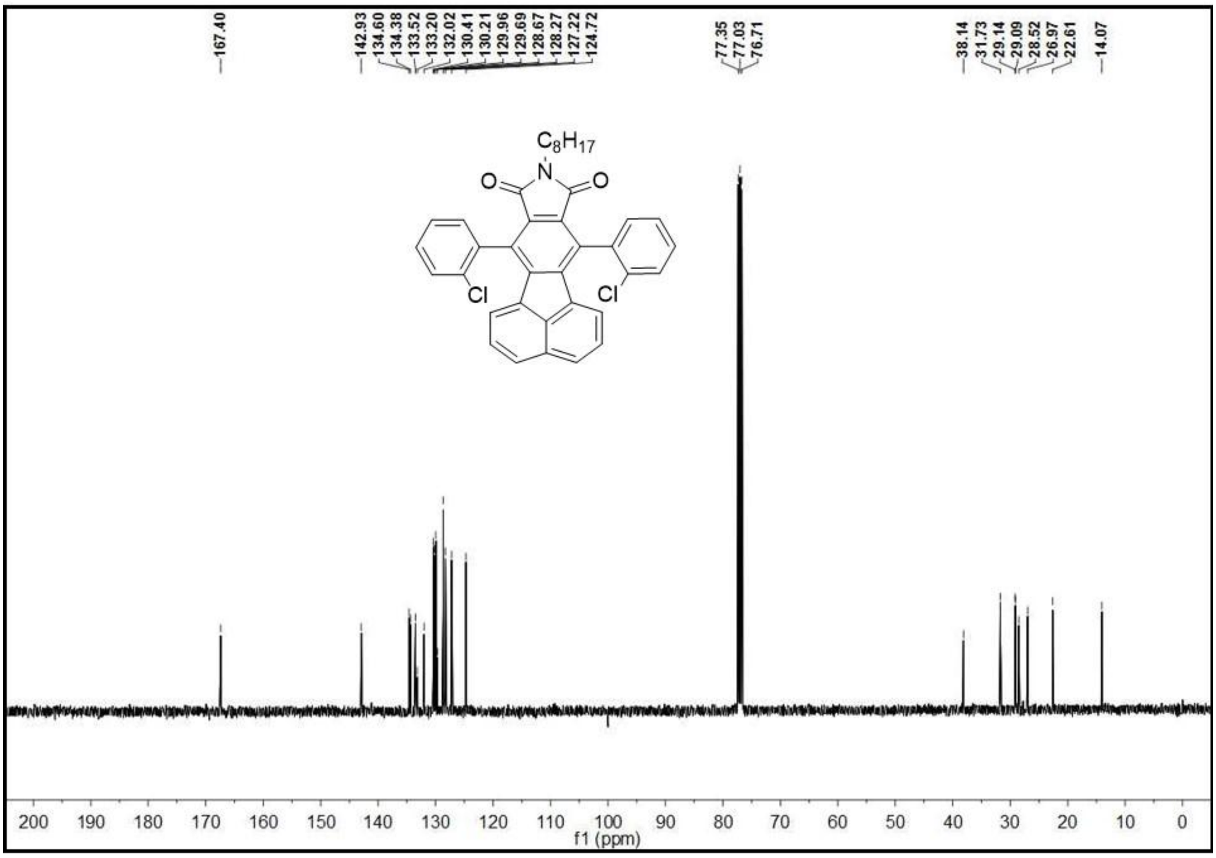
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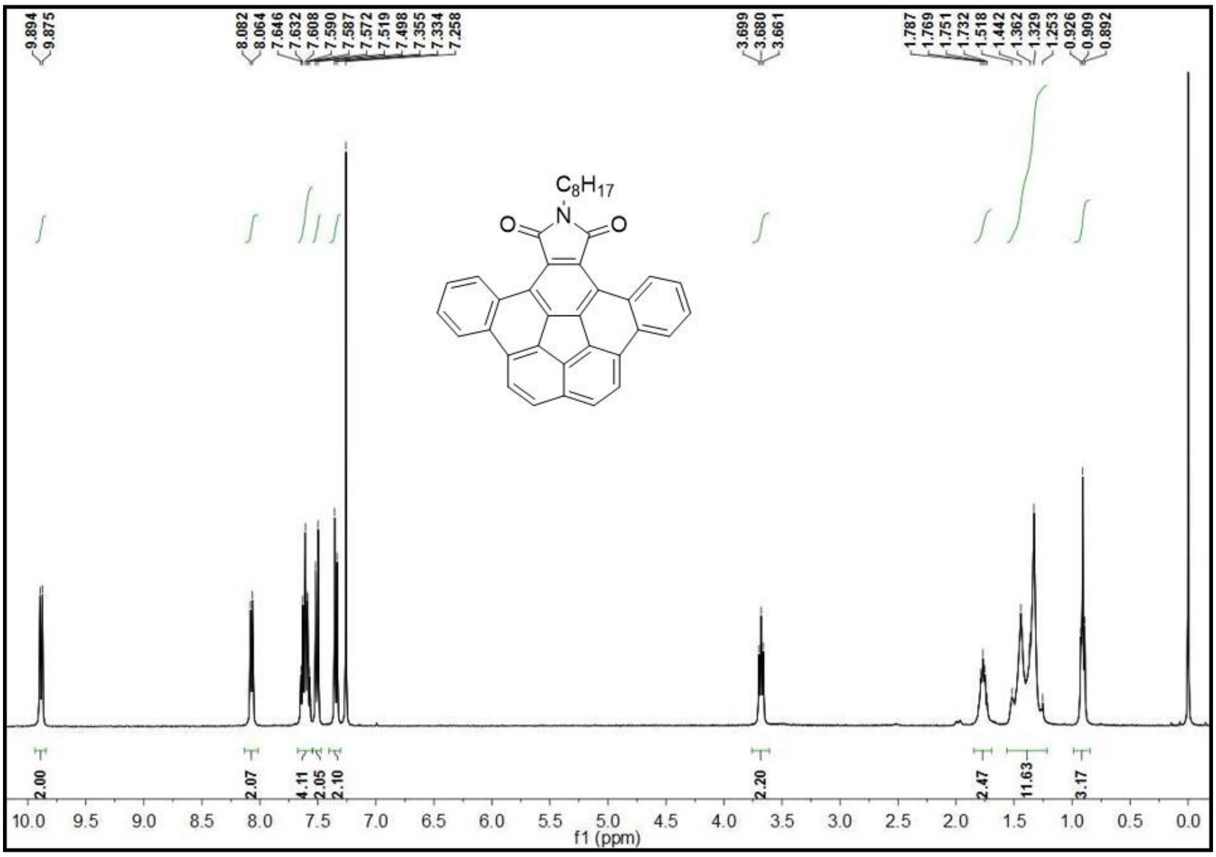
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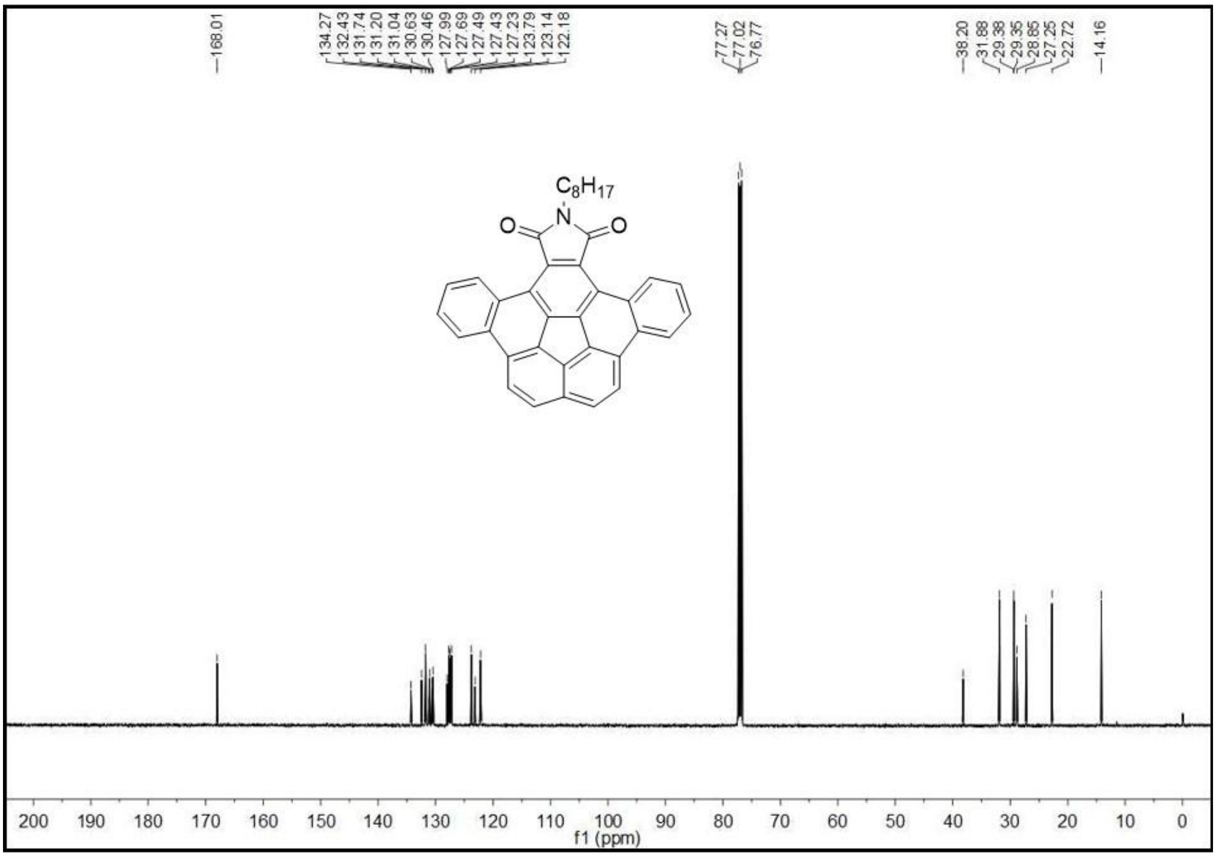
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