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Corannulene derivatives as Non-fullerene Acceptors in Solution-Processed Bulk Heterojunction Solar Cells

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1. Experimental section

General. All chemical reagents were purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX-400 (400 MHz). EI-MS mass spectra were recorded on ZAB-HS Magnetic mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer. Photoluminescence spectroscopy were recorded on HORIBA JOBIN YVON FluoroMax-4 fluorescence spectroscopy. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-*vis* spectrometer. Cyclic voltammetry (CV) was performed on CHI660D electrochemical workstation. A platinum wire was used as a counter electrode and carbon electrode as a working electrode, all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was 100 mV.s^{-1}. Atomic force microscopy studies were recorded on a Nanoscope IIIa microscope (Extended Multimode). N-hexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxabo-rolan-2-yl)phthalimide and N-hexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalimide were synthesized as previous methods[1].

1-bromocorannulene. Bromocorannulene was synthesized as reported[2]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.77 – 7.69 (m, 5H), 7.64 (d, *J* = 8.3 Hz, 1H).

Cor-PI. In a glove box, bromocorannulene(200 mg , 0.609 mmol), N-hexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phthalimide(545 mg, 1.34 mmol) and $Pd(PPh_3)_4$ (71 mg, 0.0609 mmol) were added in a sealed tube. Aliquot 336(1 mL), 0.2 M Na_2CO_3(1 mL) and toluene(40 mL) were added quickly under nitrogen out of the glove box. The solution was stirred at 130 ℃ for 24 h. The crude mixture was washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatogramphy on silica gel (DCM:PE = 1:1) to afford the title product (96 mg, 33%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.91 (s, 1H), 7.88 – 7.72 (m, 7H), 7.70 (d, *J* = 8.8 Hz, 1H), 3.73 (t, *J* = 7.3 Hz, 2H), 1.80 – 1.64 (m, 2H), 1.45 – 1.27 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.39, 168.35, 145.91, 139.39, 136.31, 136.25, 135.82, 135.77, 135.40, 135.29, 133.03, 131.13, 131.10, 131.05, 131.02, 130.41, 128.58, 127.98, 127.74, 127.58, 127.42, 127.27, 127.02, 127.00, 126.92, 126.12, 124.36, 123.54, 38.27, 31.43, 28.66, 26.60, 22.57, 14.07. MS (EI): calcd. for $C_{34}H_{25}NO_2$, $[M]^+$, 479, found 479. Elemental Anal. Calcd for $C_{34}H_{25}NO_2$: C, 85.15; H, 5.25; N, 2.92%; Found: C, 84.88; H, 5.34; N, 2.94%.

Cor-NI. In a glove box, bromocorannulene (250 mg, 0.762 mmol) N-hexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalimide(567 mg, 1.39 mmol) and $Pd(PPh_3)_4$(88 mg, 0.0762 mmol) were added in a sealed tube. Aliquot 336(1 mL), toluene(40 mL) and 0.2M Na_2CO_3(1.2 mL) were added quickly under nitrogen out of the glove box. The solution was stirred at 130 ℃ for 24 h. The crude mixture was washed with NaCl. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatogramphy on silica gel (DCM:PE = 1:1) to afford the title product (142 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.5 Hz, 1H), 8.68 (d, *J* = 6.4 Hz, 1H), 8.38 (s, 1H), 7.94 – 7.83 (m, 6H), 7.83 – 7.76 (m, 2H), 7.65-7.69 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 4.25(t, *J* = 7.6 Hz, 2H), 1.76-1.83 (m, 2H), 1.53 – 1.43 (m, 2H), 1.43 – 1.28 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.32, 164.13, 144.42, 137.70, 136.30, 135.84, 135.73, 135.71, 135.56, 133.14, 131.37, 131.22, 131.18, 130.95, 130.70, 130.40, 130.37, 129.25, 128.57, 128.51, 127.78, 127.72, 127.59, 127.50, 127.30, 127.07, 127.03, 127.01, 126.07, 122.99, 122.50, 40.61, 31.61, 28.15, 26.86, 22.61, 14.10. MS (EI): calcd. for $C_{38}H_{27}NO_2$, $[M]^+$, 529, found 529. Elemental Anal. Calcd for $C_{38}H_{27}NO_2$: C, 86.18; H, 5.14; N, 2.64%; Found: C, 86,24; H, 5.16; N, 2.62%.

2. Fig. S1-S4

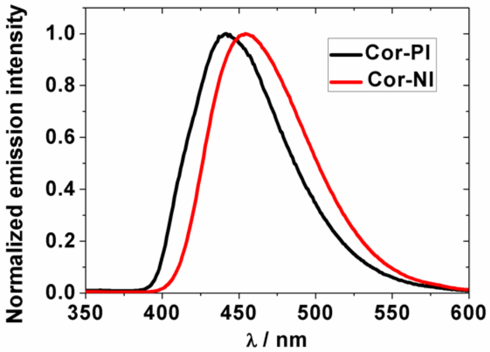


Fig. S1 Normalized emission spectra of **Cor-PI** and **Cor-NI** in CHCl$_3$.

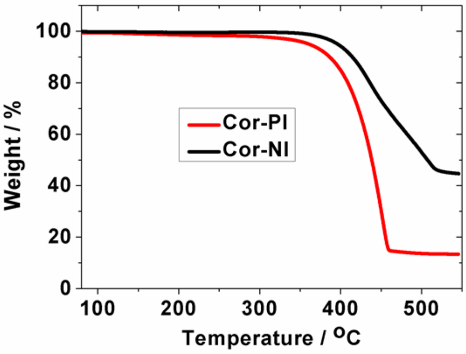


Fig. S2 TGA plot of **Cor-PI** (5% loss, 360 ^{o}C)and **Cor-NI** (5% loss, 396 ^{o}C).

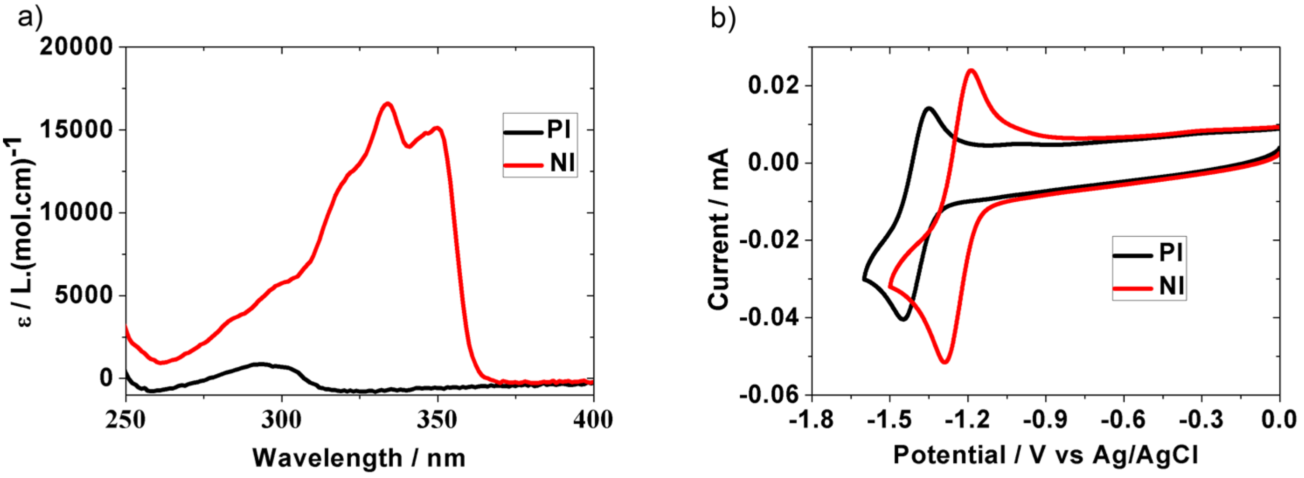


Fig. S3 a) UV-vis absorption of N-hexylphthalimide (**PI**), N-hexylnaphthalimide (**NI**) in CHCl$_3$ (1×10^{-5} M) b) Cyclic voltammograms of **PI** and **NI** in DMF.

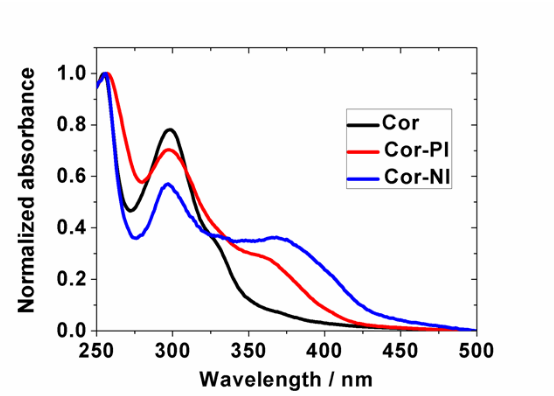


Fig. S4 UV-vis absorption of **Cor**, **Cor-PI** and **Cor-NI** in thin film (spin-coat).

3. Device fabrication and measurements

Preparation of the ZnO Precursor: Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 1 g) and ethanolamine ($NH_2CH_2CH_2OH$, 0.28 g) were dissolved in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 10 mL). Then the solution was stirred for 12 h.

Fabrication of inverted PSCs: Acetone, detergent, distilled water and isopropanol were used to clean ITO-coated glass substrates in an ultrasonic bath. Then the substrates were dried at 80 ^oC under vacuum oven for 30 min with 15 min oxygen plasma treatment followed. ZnO precursor was cast above the glass substrates at 4000 rpm for 30 s. The substrates with ZnO precursor were annealed at 150 ^oC in air and were cooled to room temperature in nitrogen-filled glove box to form ZnO amorphous films. The donor/acceptor weight ratio in P3HT and corresponding materials are 1:1 with the total concentration at 20 mg.mL^{-1}. The solution was spin-coated on the ZnO coated substrates under nitrogen atmosphere. Active layer was under room temperature overnight. The active layers were annealed at 100 ^oC for 15 min before 15 nm MoO_3 and 65 nm Ag was thermally deposited on the active layer through a shadow mask under the pressure of 3.5×10^{-4} Pa. The PCE was performed under AM 1.5G irradiation with the intensity of 100 mW cm^{-2} (Newport Solar Simulator 94021A) calibrated by a NREL certified standard silicon cell (4 cm^2). J-V curves were recorded with a Keithley 2636A semiconductor analyzer. IPCE test were carried out under monochromic illumination (Newport 74125 monochromator equipped with 66984 ARC lamp) and the calibration of the incident light intensity was performed with a calibrated silicon photodiode.

4. Computational Section

The conformational analyses of the molecular systems described in this study, including structural and orbital arrangements as well as property calculations, were carried out using the GAMESS[3] software package. Structures were fully optimized with the B97-D dispersion enabled density functional[4,5] using an ultrafine grid, in combination with the Def2-TZVPP basis set, in both gas phase and DCM solvent environment.[6] Optimized geometries were uniquely characterized via second derivatives (Hessian) analysis. Effects of solvation were taken into account using the COSab method,[7] using the dielectric for DMF and solvent radii from Klamt.[8] The calculations of HOMO/LUMO gap at the GW level have been carried out by a one-shot GW calculation on top of a DFT-LDA calculations with supercell geometries, plane wave basis sets and pseudopotentials using the QUANTUM-EXPRESSO[9] and SAX[10] software programs, with the following approximations: Godby-Needs plasmon pole approximation[11] for energy dependence of the screened Coulomb potential, standard BSE with static approximation to the screened Coulomb potential plus Tamm-Dancoff approximation.[12] A cut-off of 70 ry (45 ry) for the electronic wave-function and the Fock operator for molecules including N and O atoms in addition to C/H atoms (only including C/H atoms) has been used. A cut-off of 2 ry has been used for the evaluation of the polarizability. The GW and HF quasiparticle energies were obtained in a perturbation scheme from the DFT-LDA Kohn Sham eigenvalues. The Martyna-Tuckerman method was applied to avoid replica interactions. Visualization and analysis of structural and property results, including electrophilic (HOMO) and nucleophilic (LUMO) frontier density plots, were obtained using Avagadro[13] and WEBMO.[14]

4.1. Optimized structures of Cor-PI and Cor-NI.

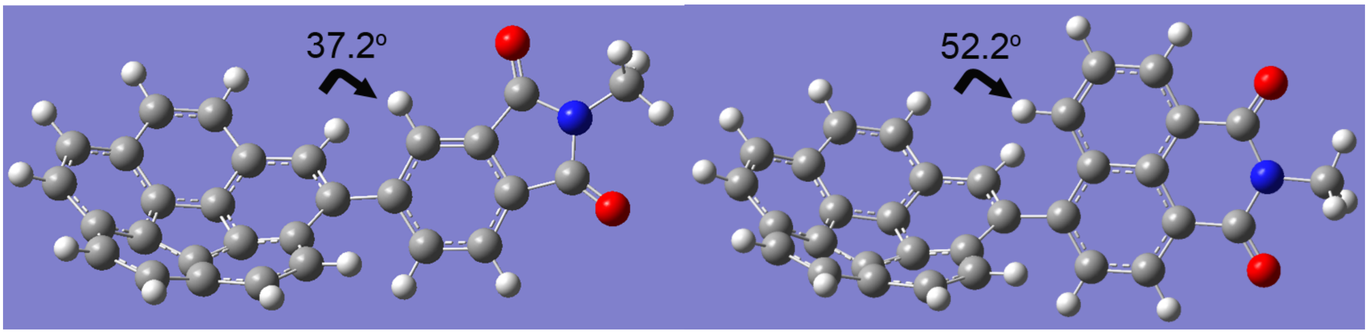


Fig. S5 Optimized structures and dihedral angle between the benzene ring linking with imides and imides moieties of **Cor-PI** and **Cor-NI**.

4.2. Calculated molecular orbitals.

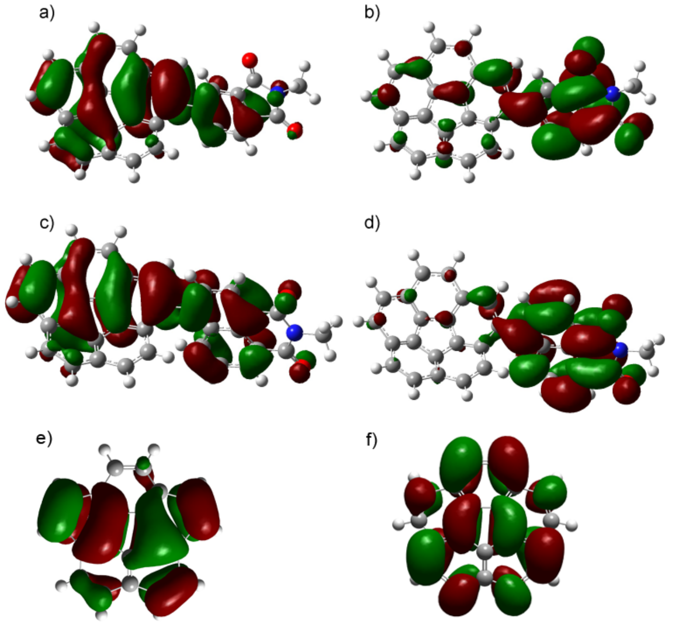


Fig. S6 Calculated molecular orbitals of **Cor-PI** and **Cor-NI**. a), b) HOMO and LUMO of **Cor-PI**. c), d) HOMO and LUMO of **Cor-NI**. e), f) HOMO and LUMO of **Cor**.

4.3. Electrophilic HOMO plot and nucleophilic LUMO plot of Cor-PI and Cor-NI.

Concave side Convex side

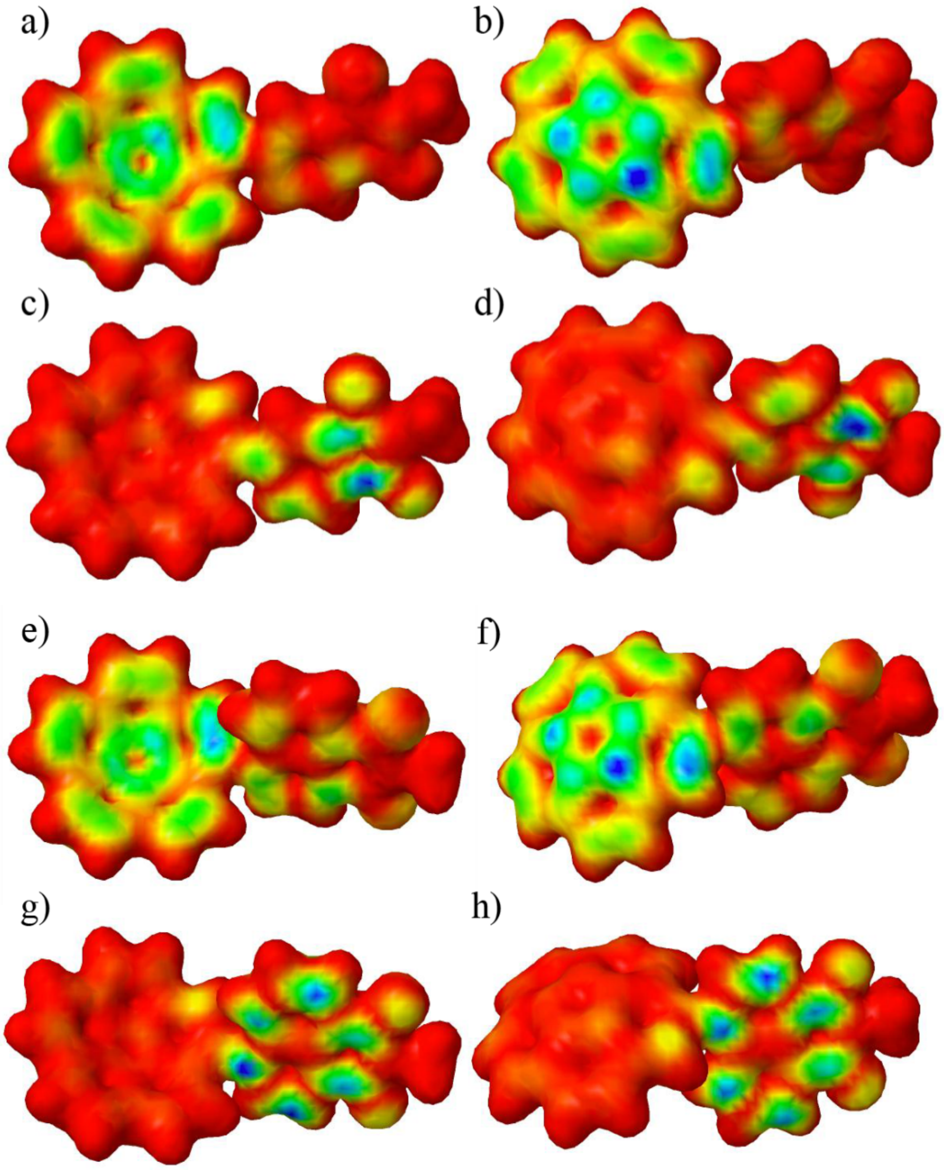


Fig. S7 (a), (b) Electrophilic HOMO plot of **Cor-PI**, 0.02 (blue is highest probability of attack by an electrophile). (c), (d) Nucleophilic LUMO plot of **Cor-PI**, 0.02 (blue is highest probability of attack by a nucleophile). (e), (f) Electrophilic HOMO plot of **Cor-NI**, 0.02 (blue is highest probability of attack by an electrophile). (g), (h) Nucleophilic LUMO plot of **Cor-NI**, 0.02 (blue is highest probability of attack by a nucleophile)

4.4. Calculated properties of Cor, Cor-PI and Cor-NI(B97D/Def2-TZVPP).

Table S1

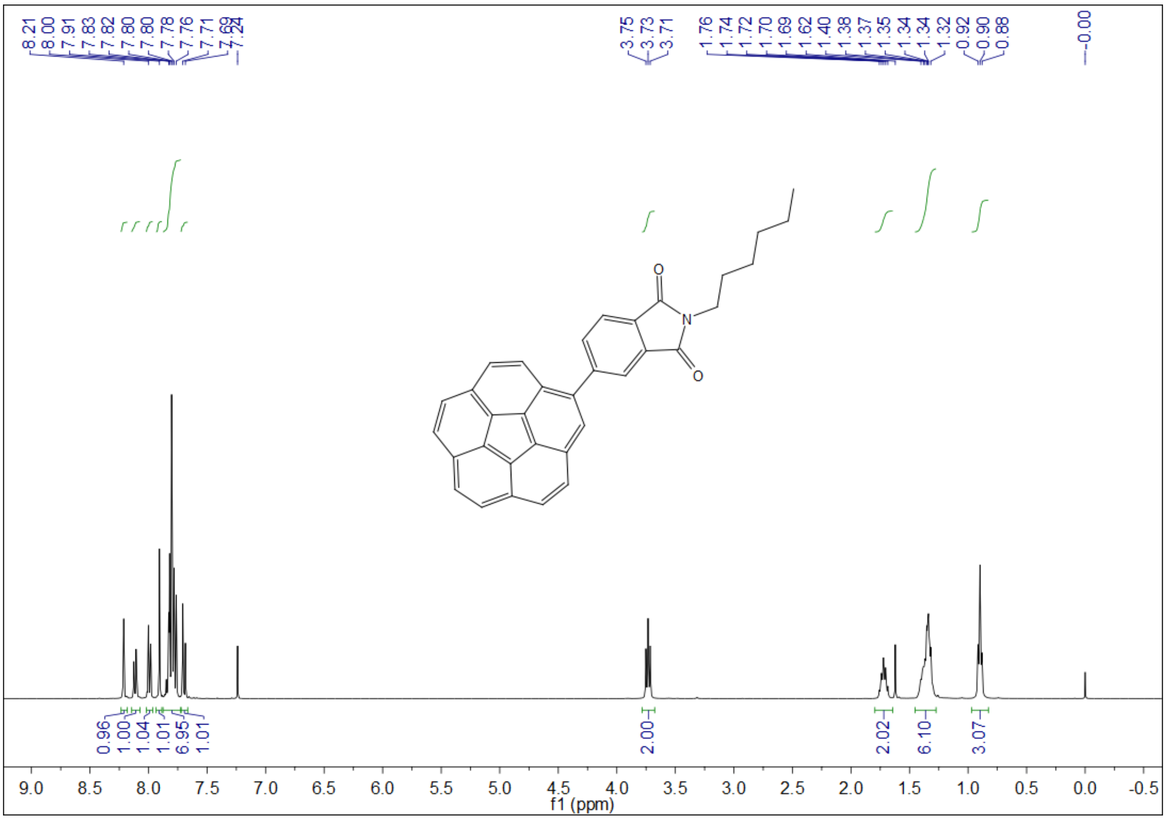
Compound	E_b[2] (gas phase)	E_b[2] (DCM)[1]	Bowl Depth (gas phase)	Bowl Depth (DCM)[1]	GW H/L gap[3]
Cor	10.57	10.90	0.916	0.922	7.3
Cor-PI	10.78	11.08	0.913	0.917	7.2
Cor-NI	10.67	10.94	0.915	0.921	6.6

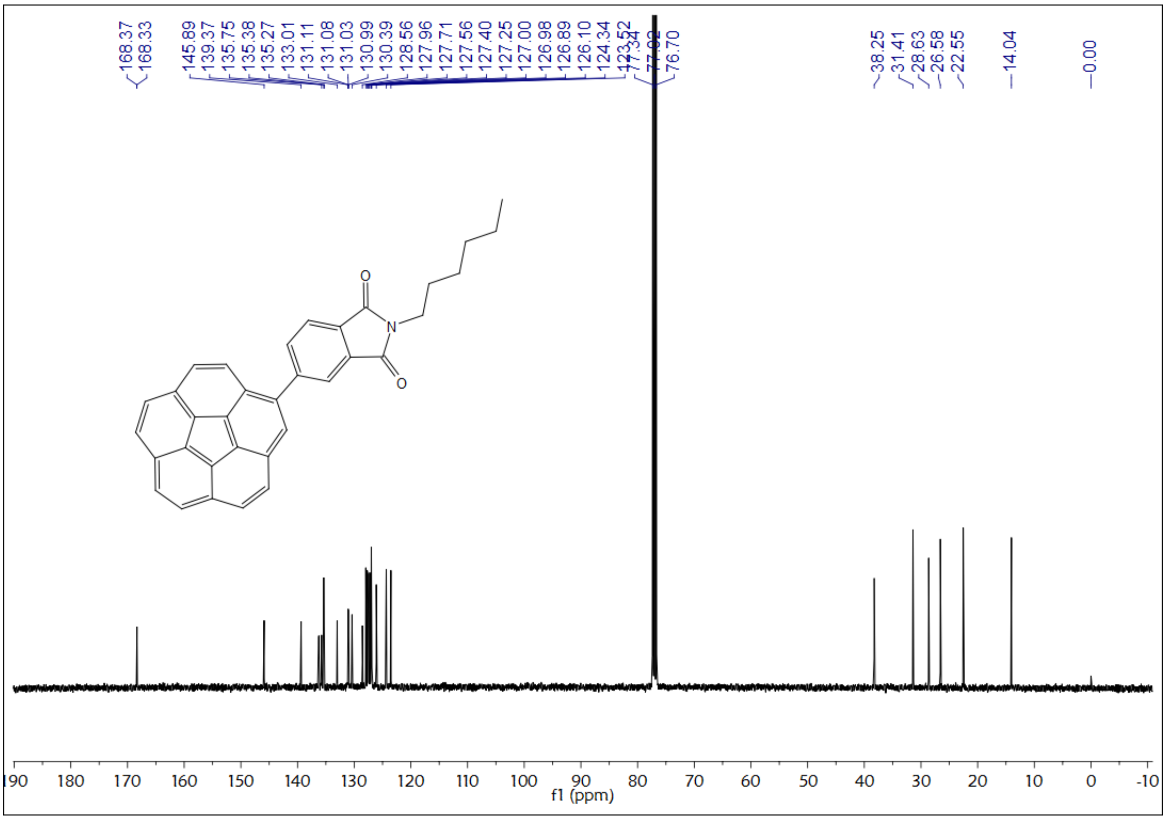
[1] In dichloromethane

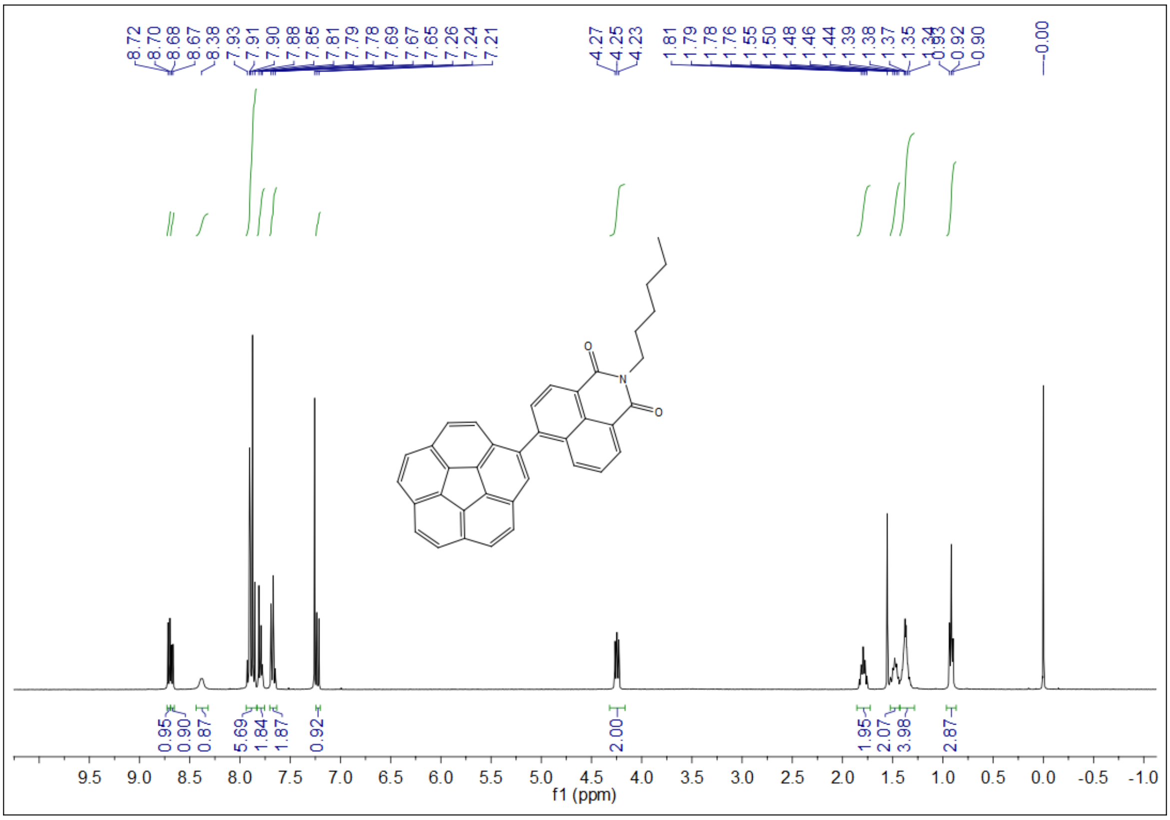
[2] Barrier to bowl-to-bowl interconversion

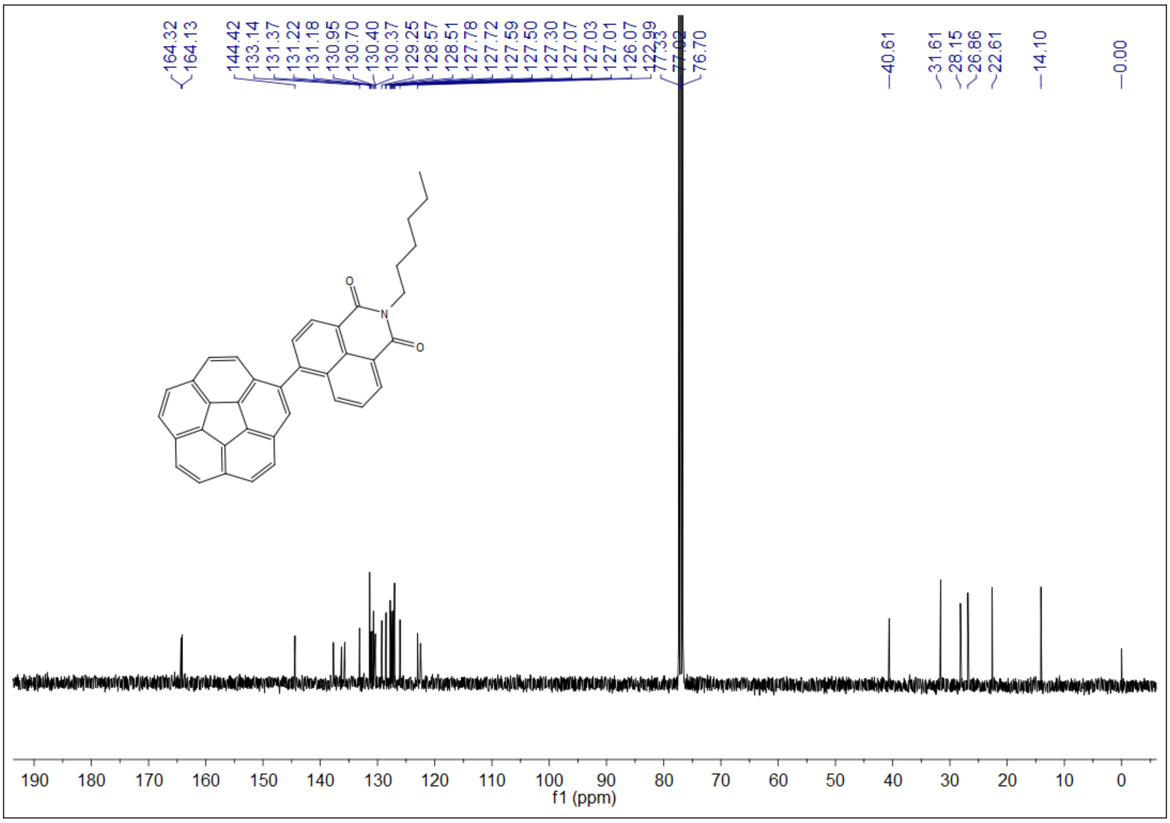
[3] In gas phase

5. NMR spectra


8.21
8.00
7.91
7.83
7.82
7.80
7.80
7.78
7.76
7.71
7.69
7.24
3.75
3.73
3.71
1.76
1.74
1.72
1.70
1.69
1.62
1.40
1.38
1.37
1.35
1.34
1.32
0.92
0.90
0.88
0.00
O
N
O
0.96
1.00
1.04
1.01
6.95
1.01
2.00
2.02
6.10
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.37
168.33
145.89
139.37
135.75
135.38
135.27
133.01
131.11
131.08
131.03
130.99
130.39
128.56
127.96
127.71
127.56
127.40
127.25
127.00
126.98
126.89
126.10
124.34
123.52
77.34
77.02
76.70
38.25
31.41
28.63
26.58
22.55
14.04
0.00
O
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)





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