Supporting Information for

Combinatorial Selection Among Geometrical Isomers of Discrete Long Carbon Chain-Naphthalenediimides Induces Local Order at the Liquid/Solid Interface

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Synthesis and characterization

Compounds **1**,[S1] **2**,[S2] **3**,[S2] **4**,[S1] **5**, [S1] **6**,[S1] **7**,[S1] **8**,[S1] **9**,[S1] and **10**[S1] were synthesized as previously described.

nonatriaconta-6,17-dien-1-amine (u_2C_{39}-NH_2)

Compound **2** (1.04 g; 2.58 mmol) was dissolved in dry THF (8 mL). Finely ground dry K_2CO_3 (720 mg; 5.21 mmol) was added, followed by **7** (1.02 g; 2.14 mmol) and 18-Crown-6 (0.071 g; 0.268 mmol). The mixture was heated at reflux for 29 h, after which ^{1}H NMR analysis revealed full conversion. The solvent was removed and the crude product was stirred with heptane (100 mL) for one hour. The obtained solid was filtered (folded paper filter), and the filter washed thoroughly twice with heptane (50 mL). The combined heptane solutions were washed with CH_3CN (5 × 50 mL). Removal of heptane yielded 0.95 g of crude product, which was purified by column chromatography (Grace Reveleris X2, 24g HP-Sil Buchi column, heptane-EtOAc, from 0% to 18% EtOAc). Column chromatography afforded 0.767 g of impure **u_2C_{39}NHBoc**. The obtained compound was dissolved in $CHCl_3$ (6 mL) under an Ar atmosphere. TFA (2 mL) was added, and the resulting solution was stirred for 4 h at room temperature. The mixture was diluted with $CHCl_3$ (50 mL) and extracted with aq. 1M NaOH (50 mL). The organic phase was washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered and dried, obtaining 0.636 g of crude product. Purification with column chromatography (Grace Reveleris X2, 24g Buchi SiO_2 column, 7:3 $CHCl_3$/EtOAc to remove the impurities; the addition of 5% *iso*-propylamine to the eluent mixture allowed the elution of the amine) afforded **$u_2C_{39}NH_2$** (0.276 g; 0.492 mmol; 23% yield).

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 5.38-5.32 (m, 4H), 2.68 (t, *J* = 6 Hz, 2H), 2.04-1.95 (m, 8H), 1.44-1.25 (m, 60H), 0.88 (t, *J* = 6 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 130.73, 130.51, 130.47, 130.24, 130.21, 130.05, 130.01, 129.74, 42.38, 33.93, 33.88, 32.76, 32.70, 32.08, 29.93, 29.92, 29.86, 29.81, 29.78, 29.76, 29.72, 29.68, 29.65, 29.63, 29.56, 29.52, 29.48, 29.33, 27.38, 27.36, 27.32, 26.69, 26.54, 22.84, 14.27.

FT-IR (dry powder) (cm^{-1}): 3351 (*N-H*), 3004 (C=*C-H*), 2915 (*C-H*), 2846 (*C-H*).

MALDI-TOF MS (*m/z*): $[M+H]^+$ calcd for $C_{39}H_{78}N$ 560.61; found 560.64.

M_p (DSC): three thermal transitions observed at 34.7 ºC, 42.0 ºC and 55.0 ºC. Above 58 ºC all the material is in the molten state.

tetratetraconta-11,22-dien-1-amine (u_2C_{44}-NH_2)

Compound **3** (2.27 g; 3.54 mmol) was dissolved in dry THF (15 mL). Finely ground dry K_2CO_3 (1.13 g; 8.17 mmol) was added, followed by **7** (1.30 g; 2.73 mmol) and 18-Crown-6 (0.074 g; 0.280 mmol). The mixture was heated up to reflux for 25 h, after which ^{1}H NMR analysis revealed full conversion. The solvent was removed and the crude product was stirred with heptane (100 mL) for one hour. The obtained solid was filtered (folded paper filter), and the filter washed thoroughly twice with heptane (25 mL). The combined heptane solutions were washed with CH_3CN (5 × 50 mL). Removal of heptane yielded 1.37 g of crude product, which was purified by column chromatography (Grace Reveleris X2, 24g HP-Sil Buchi column, heptane-EtOAc, from 0% to 18% EtOAc). Column chromatography afforded 0.724 g of impure **u_2C_{44}NPhth**. The obtained compound was loaded in a Schlenk flask and a 33% ethanol solution of methylamine (6 mL) was added under an Ar atmosphere. The mixture was heated at 80ºC for 18 h. The hot solution was allowed to cool down to room temperature and, after standing for several h, crystallization occurred. The precipitate was filtered off with suction, washed with EtOH (20 mL) and dried, affording a white solid. Purification with column chromatography (Grace Reveleris X2, 24g Buchi SiO_2 column, 7:3 $CHCl_3$/EtOAc to remove the impurities; the addition of 5% *iso*-propylamine to the eluent mixture allowed the elution of the amine) afforded **$u_2C_{44}NH_2$** (0.394 g; 0.625 mmol; 23% yield).

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 5.38-5.32 (m, 4H), 2.68 (t, *J* = 6 Hz, 2H), 2.03-1.94 (m, 8H), 1.44-1.25 (m, 70H), 0.88 (t, *J* = 6 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 130.52, 130.51, 130.49, 130.06, 130.05, 130.03, 42.44, 34.04, 32.76, 32.08, 29.93, 29.86, 29.81, 29.80, 29.78, 29.75, 29.72, 29.68, 29.52, 29.47, 29.33, 27.36, 27.06, 22.85, 14.27.

FT-IR (dry powder) (cm^{-1}): 3258 (*N-H*), 3169 (*N-H*), 3005 (C=*C-H*), 2915 (*C-H*), 2848 (*C-H*).

MALDI-TOF MS (*m/z*): $[M+H]^+$ calcd for $C_{44}H_{88}N$ 630.69; found 630.74

M_p (DSC): two thermal transitions observed at 33.7 ºC and 54.8 ºC. Above 56 ºC all the material is in the molten state.

pentaconta-6,17,28-trien-1-amine (u_3C_{50}-NH_2)

Compound **10** (0.80 g; 1.273 mmol) and 18-Crown-6 (0.060 g; 0.227 mmol) were dissolved in dry THF (8 mL). Finely ground dry K_2CO_3 (0.558 g; 5.21 mmol) was added, followed by **2** (0.97 g; 1.782 mmol). The mixture was heated at reflux for 69 h, after which ^{1}H NMR analysis revealed full conversion. The solvent was removed and the crude product was stirred with heptane (100 mL) for two h. The obtained solid was filtered (folded paper filter), and the filter

washed thoroughly twice with heptane (50 mL). The combined heptane solutions were washed with CH_3CN (7 × 25 mL). Removal of heptane yielded 0.77 g of crude product, which was purified by column chromatography (Grace Reveleris X2, 24g HP-Sil Buchi column, heptane-EtOAc, from 0% to 18% EtOAc). Column chromatography afforded 0.617 g of impure **u_3C_{50}NHBoc**. The obtained compound was dissolved in $CHCl_3$ (6 mL) under an Ar atmosphere. TFA (2 mL) was added, and the resulting solution was stirred for 4 h at room temperature. The mixture was diluted with $CHCl_3$ (100 mL) and extracted with aq. 1M NaOH (100 mL). The organic phase was washed with H_2O (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered and dried, obtaining 0.600 g of crude product. Purification with column chromatography (Grace Reveleris X2, 24g Buchi SiO_2 column, 7:3 $CHCl_3$/EtOAc to remove the impurities; the addition of 5% *iso*-propylamine to the eluent mixture allowed the elution of the amine) afforded **$u_3C_{50}NH_2$** (0.457 g; 0.641 mmol; 50% yield).

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 5.38-5.32 (m, 6H), 2.68 (t, *J* = 6 Hz, 2H), 2.04-1.95 (m, 12H), 1.47-1.25 (m, 74H), 0.88 (t, *J* = 6 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 130.73, 130.52, 130.49, 130.25, 130.22, 130.05, 130.04, 130.02, 129.76, 42.38, 33.94, 33.89, 32.76, 32.70, 32.08, 30.04, 29.93, 29.85, 29.81, 29.78, 29.76, 29.72, 29.68, 29.64, 29.63, 29.55, 29.52, 29.48, 29.33, 27.38, 27.36, 27.32, 26.69, 26.54, 22.84.

FT-IR (dry powder) (cm^{-1}): 3351 (*N-H*), 3004 (C=*C-H*), 2915 (*C-H*), 2846 (*C-H*).

MALDI-TOF MS (*m/z*): $[M+H]^+$ calcd for $C_{50}H_{98}N$ 712.77; found 712.78.

M_p (DSC): two thermal transitions observed at 32.8 ºC and 50.8 ºC. Above 52 ºC all the material is in the molten state.

pentapentaconta-11,22,33-trien-1-amine (u_3C_{55}-NH_2)

Compound **3** (1.28 g; 2.00 mmol) was dissolved in dry THF (10 mL). A 1M THF solution of *t*-BuOK (2.20 mL; 2.20 mmol), after which the solution turned dark red. After 5 min, a THF solution (10 mL) of 18-Crown-6 (0.022 g; 0.08 mmol) and **10** (0.90 g; 1.43 mmol) was added dropwise during 5 min. The mixture was stirred at room temperature for 18 h, after which ^{1}H NMR analysis revealed full conversion. The solvent was removed and the crude product was stirred with heptane (100 mL) for one hour. The obtained solid was filtered (folded paper filter), and the filter washed thoroughly with twice with heptane (25 mL). The combined heptane solutions were washed with CH_3CN (5 × 50 mL). Removal of heptane yielded 1.63 g of crude product (oil). The crude product was dissolved in boiling EtOH (150 mL). After cooling down to room temperature, the solution was stored overnight in the fridge, and precipitation occurred.

The solid was filtered and washed with ice-cold EtOH (50 mL) to obtain a white solid (1.01 g). The crude material was further purified by column chromatography (Grace Reveleris X2, 40g HP-Sil Buchi column, heptane-EtOAc, from 0% to 8% EtOAc). Column chromatography afforded 0.760 g of impure **u$_3$C$_{55}$NPhth**. The obtained compound was loaded in a Schlenk flask and a 33% ethanol solution of methylamine (6 mL) was added under an Ar atmosphere. The mixture was heated at 80ºC for 18 h. The hot solution was allowed to cool down to room temperature and, after standing for several h, crystallization occurred. The precipitate was filtered off with suction, washed with EtOH (20 mL) and dried, affording a white solid (0.32 g). Purification by column chromatography (Grace Reveleris X2, 24g Buchi SiO_2 column, 7:3 $CHCl_3$/EtOAc to remove the impurities; the addition of 5% *iso*-propylamine to the eluent mixture allowed the elution of the amine) afforded **u$_3$C$_{55}$NH$_2$** (0.267 g; 0.341 mmol; 24% yield).

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 5.38-5.32 (m, 6H), 2.68 (t, *J* = 6 Hz, 2H), 2.04-1.94 (m, 12H), 1.45-1.25 (m, 84H), 0.88 (t, *J* = 6 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 130.50, 130.49, 130.05, 130.04, 130.02, 42.43, 34.06, 32.77, 32.08, 29.93, 29.86, 29.82, 29.80, 29.78, 29.75, 29.72, 29.68, 29.56, 29.52, 29.48, 29.33, 27.36, 27.06, 22.85.

FT-IR (dry powder) (cm^{-1}): 3351 (*N-H*), 3003 (C=*C-H*), 2915 (*C-H*), 2846 (*C-H*).

MALDI-TOF MS (*m/z*): $[M+H]^+$ calcd for $C_{55}H_{108}N$ 782.85; found 782.88.

M_p (DSC): two thermal transitions observed at 41.6 ºC and 58.6 ºC. Above 60 ºC all the material is in the molten state.

General procedure for the synthesis of unsaturated C_n-NDI-C_n.

NDA (1 eq) and the desired unsaturated amine (2 eq) were suspended in a DMF:THF mixture (6 mL and 5 mL, respectively) in a microwave vial. The suspension was sonicated for 5 min, the vial was sealed and the mixture was heated at 75 ºC for 5 min, followed by 20 min at 140 ºC. The mixture was cooled down and poured in aq. 1M NaOH (200 mL) to induce precipitation. The solid was filtered by suction and dried. The crude material was purified by column chromatography (SiO_2, heptane/$CHCl_3$ from 0% to 100% $CHCl_3$) to afford the unsaturated **C_n-NDI-C_n** as white solids.

u2C39-NDI-u2C39

(315 mg; 0.23 mmol; 78% yield)

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 8.75 (s, 4H), 5.39-5.32 (m, 8H), 4.19 (t, *J* = 6 Hz, 4H), 2.07-1.95 (m, 16H), 1.75 (p, *J* = 6 Hz, 4H), 1.46-1.42 (m, 8H), 1.33-1.25 (m, 104H), 0.88 (t, *J* = 6 Hz, 6H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 162.95, 131.07, 130.91, 130.51, 130.48, 130.42, 130.05, 130.02, 129.99, 129.52, 126.85, 126.79, 41.08, 32.76, 32.58, 32.08, 29.93, 29.86, 29.82, 29.79, 29.73, 29.69, 29.65, 29.56, 29.52, 29.50, 29.48, 29.42, 29.37, 29.34, 28.14, 28.07, 27.39, 27.36, 27.22, 26.88, 26.69, 22.85, 14.27.

FT-IR (dry powder) (cm^{-1}): 3004 (C=*C-H*), 2916 (*C-H*), 2849 (*C-H*), 1656 (*C=O*).

MALDI-TOF MS (*m/z*): $[M^{\bullet}]^-$ calcd for $C_{92}H_{154}N_2O_4$ 1351.19; found 1351.17.

M_p (DSC): 68.4 ºC.

u2C44-NDI-u2C44

(313 mg; 0.21 mmol; 85% yield)

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 8.75 (s, 4H), 5.38-5.31 (m, 8H), 4.19 (t, *J* = 6 Hz, 4H), 2.02-1.94 (m, 16H), 1.74 (p, *J* = 6 Hz, 4H), 1.45-1.40 (m, 4H), 1.37-1.25 (m, 128H), 0.88 (t, *J* = 6 Hz, 6H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 162.97, 131.07, 130.51, 130.49, 130.48, 130.05, 130.03, 130.01, 126.85, 126.80, 41.15, 32.77, 32.08, 29.93, 29.86, 29.82, 29.78, 29.72, 29.69, 29.65, 29.52, 29.48, 29.35, 29.33, 28.24, 27.37, 27.25, 22.85, 14.28.

FT-IR (dry powder) (cm^{-1}): 3004 (C=*C-H*), 2916 (*C-H*), 2849 (*C-H*), 1655 (*C=O*).

MALDI-TOF MS (*m/z*): $[M^{\bullet}]^-$ calcd for $C_{102}H_{174}N_2O_4$ 1491.34; found 1491.32.

M_p (DSC): 73.4 ºC.

u_3C_{50}-NDI-u_3C_{50}

(250 mg; 0.15 mmol; 80% yield)

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 8.76 (s, 4H), 5.39-5.32 (m, 12H), 4.19 (t, *J* = 6 Hz, 4H), 2.07-1.94 (m, 24H), 1.75 (p, *J* = 6 Hz, 4H), 1.47-1.42 (m, 8H), 1.33-1.25 (m, 132H), 0.88 (t, *J* = 6 Hz, 6H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 162.95, 131.07, 130.91, 130.52, 130.49, 130.42, 130.06, 130.03, 129.52, 126.85, 126.80, 41.08, 32.77, 32.08, 29.93, 29.86, 29.82, 29.78, 29.74, 29.72, 29.69, 29.57, 29.52, 29.51, 29.48, 29.42, 29.38, 29.35, 29.34, 28.15, 27.40, 27.37, 27.23, 26.89, 22.85, 14.28.

FT-IR (dry powder) (cm^{-1}): 3005 (C=*C-H*), 2916 (*C-H*), 2849 (*C-H*), 1655 (*C=O*).

MALDI-TOF MS (*m/z*): $[M^{\bullet}]^-$ calcd for $C_{114}H_{194}N_2O_4$ 1655.50; found 1655.52.

M_p (DSC): 55.5 ºC.

u_3C_{55}-NDI-u_3C_{55}

(287 mg; 0.16 mmol; 75% yield)

^{1}H-NMR ($CDCl_3$, 600 MHz, δ): 8.75 (s, 4H), 5.38-5.31 (m, 12H), 4.19 (t, *J* = 6 Hz, 4H), 2.02-1.94 (m, 24H), 1.74 (p, *J* = 6 Hz, 4H), 1.45-1.40 (m, 4H), 1.36-1.25 (m, 156H), 0.88 (t, *J* = 6 Hz, 6H).

^{13}C-NMR ($CDCl_3$, 150 MHz, δ): 162.97, 131.07, 130.51, 130.49, 130.48, 130.05, 130.03, 130.01, 126.85, 126.80, 41.15, 32.77, 32.08, 29.93, 29.86, 29.82, 29.78, 29.73, 29.69, 29.65, 29.59, 29.52, 29.48, 29.34, 28.25, 27.37, 27.25, 22.85, 14.28.

FT-IR (dry powder) (cm^{-1}): 3004 (C=*C-H*), 2916 (*C-H*), 2849 (*C-H*), 1656 (*C=O*).

MALDI-TOF MS (*m/z*): $[M^{\bullet}]^-$ calcd for $C_{124}H_{214}N_2O_4$ 1795.66; found 1795.66.

M_p (DSC): 62.1 ºC.

General procedure for the synthesis of saturated C_n-NDI-C_n.

The desired unsaturated **C_n-NDI-C_n** (1 eq) was weighed in a 5 mL round bottom flask and suspended in a 2:1 toluene/ethyl valerate mixture (3 mL). The solution was purged with N_2, Pd/C 10 wt% (15 mg) was added, the reflux condenser was mounted and the flask was sealed under N_2. A H_2 balloon was connected to the setup, and the atmosphere was saturated with H_2. The mixture was stirred and heated at the appropriate temperature (see Table S1) for 3 h. The solvent was removed and the crude product was loaded on a Soxhlet cartridge. A Soxhlet extraction with the adequate solvent (see Table S1) was carried out overnight. The extracted solution was cooled down. Upon cooling a white solid precipitated. The precipitate was filtered, washed with pentane and dried under vacuum to afford saturated **C_n-NDI-C_n** as white solid.

Table S1. Reaction conditions applied in the Pd-catalyzed hydrogenation of the unsaturated **C_n-NDI-C_n**.

Synthesized Compound	Reaction temperature (ºC)	Solvent for Soxhlet extraction
C_{39}-NDI-C_{39}	110 ºC	*n*-heptane
C_{44}-NDI-C_{44}	110 ºC	*n*-heptane
C_{50}-NDI-C_{50}	115 ºC	*n*-octane

2,7-dinonatriacontylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (C_{39}-NDI-C_{39})

(100 mg; 0.07 mmol; 90% yield)

^{1}H-NMR ($Cl_2CDCDCl_2$, 500 MHz, 85 ºC, δ): 8.77 (s, 4H), 4.23 (t, *J* = 7 Hz, 4H), 1.81 (p, *J* = 8 Hz, 4H), 1.48-1.32 (m, 144H), 0.94 (t, *J* = 7 Hz, 6H).

^{13}C-NMR ($Cl_2CDCDCl_2$, 125 MHz, 85 ºC, δ): 162.55, 130.61, 126.59, 40.86, 31.68, 29.46, 29.44, 29.40, 29.36, 29.30, 29.09, 29.07, 27.95, 26.92, 22.41, 13.81.

FT-IR (dry powder) (cm^{-1}): 2917 (*C-H*), 2848 (*C-H*), 1656 (*C=O*).

M_p (DSC): 132.4 ºC.

2,7-ditetratetracontylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (C_{44}-NDI-C_{44})

(90 mg; 0.06 mmol; 92% yield)

^{1}H-NMR ($Cl_2CDCDCl_2$, 500 MHz, 85 ºC, δ): 8.77 (s, 4H), 4.23 (t, J = 7 Hz, 4H), 1.81 (p, J = 7 Hz, 4H), 1.48-1.23 (m, 164H), 0.94 (t, J = 7 Hz, 6H).

^{13}C-NMR ($Cl_2CDCDCl_2$, 125 MHz, 85 ºC, δ): 162.54, 130.61, 126.59, 40.86, 31.68, 29.44, 29.40, 29.35, 29.30, 29.09, 29.07, 27.95, 26.92, 22.41, 13.81.

FT-IR (dry powder) (cm^{-1}): 2916 (*C-H*), 2848 (*C-H*), 1657 (*C=O*).

M_p (DSC): 128.7 ºC.

2,7-dipentacontylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (C_{50}-NDI-C_{50})

(150 mg; 0.09 mmol; 87% yield)

^{1}H-NMR ($Cl_2CDCDCl_2$, 500 MHz, 85 ºC, δ): 8.77 (s, 4H), 4.23 (t, J = 7 Hz, 4H), 1.81 (p, J = 7 Hz, 4H), 1.48-1.32 (m, 188H), 0.94 (t, J = 7 Hz, 6H).

^{13}C-NMR ($Cl_2CDCDCl_2$, 125 MHz, 85 ºC, δ): 162.54, 130.61, 126.59, 40.86, 31.68, 29.45, 29.40, 29.36, 29.31, 29.09, 29.07, 27.96, 26.93, 22.42, 13.81.

FT-IR (dry powder) (cm^{-1}): 2916 (*C-H*), 2848 (*C-H*), 1656 (*C=O*).

M_p (DSC): 131.7 ºC.

^{1}H NMR and ^{13}C NMR spectra

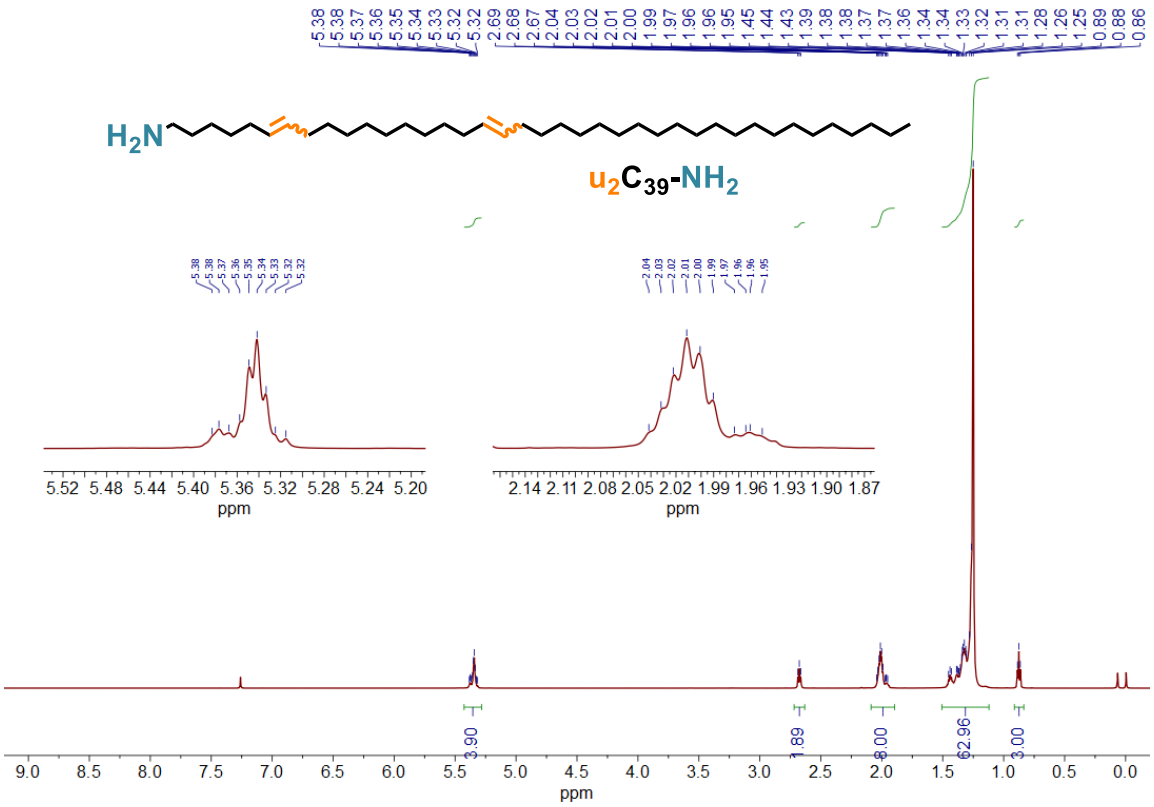

Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **u$_2$C$_{39}$NH$_2$.**

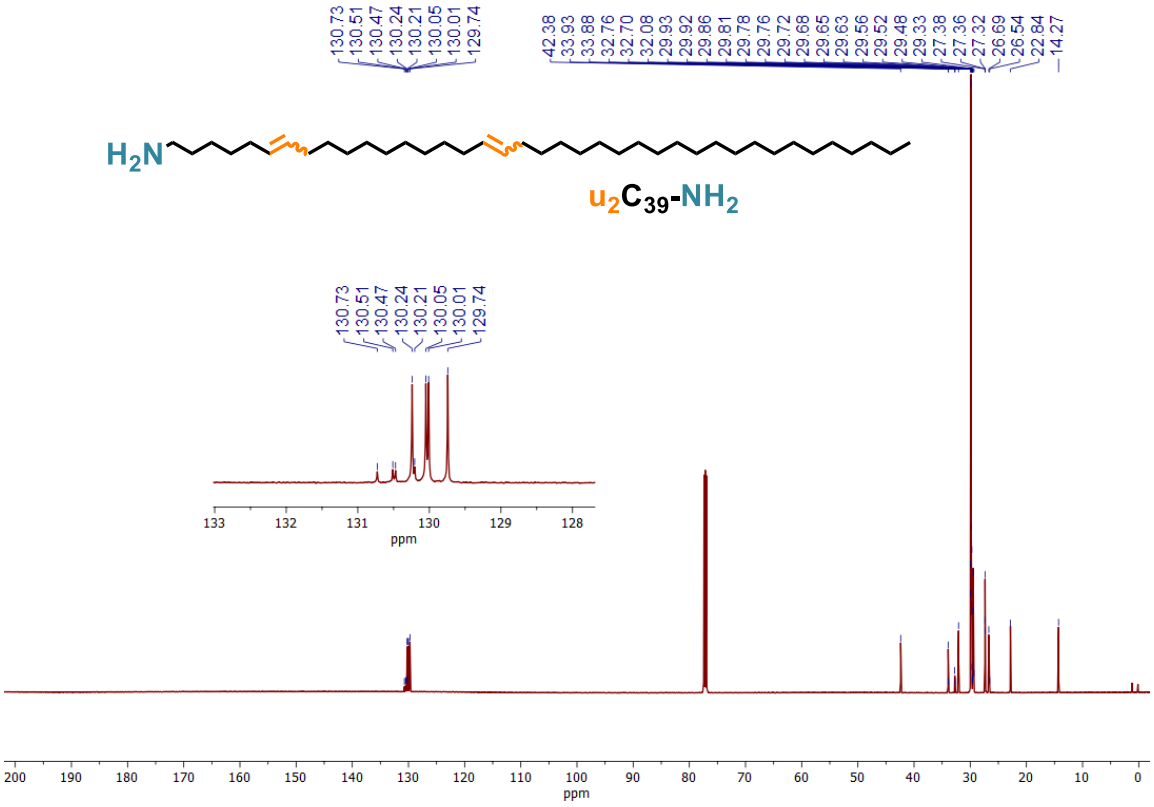

Figure S2. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **u$_2$C$_{39}$NH$_2$.**

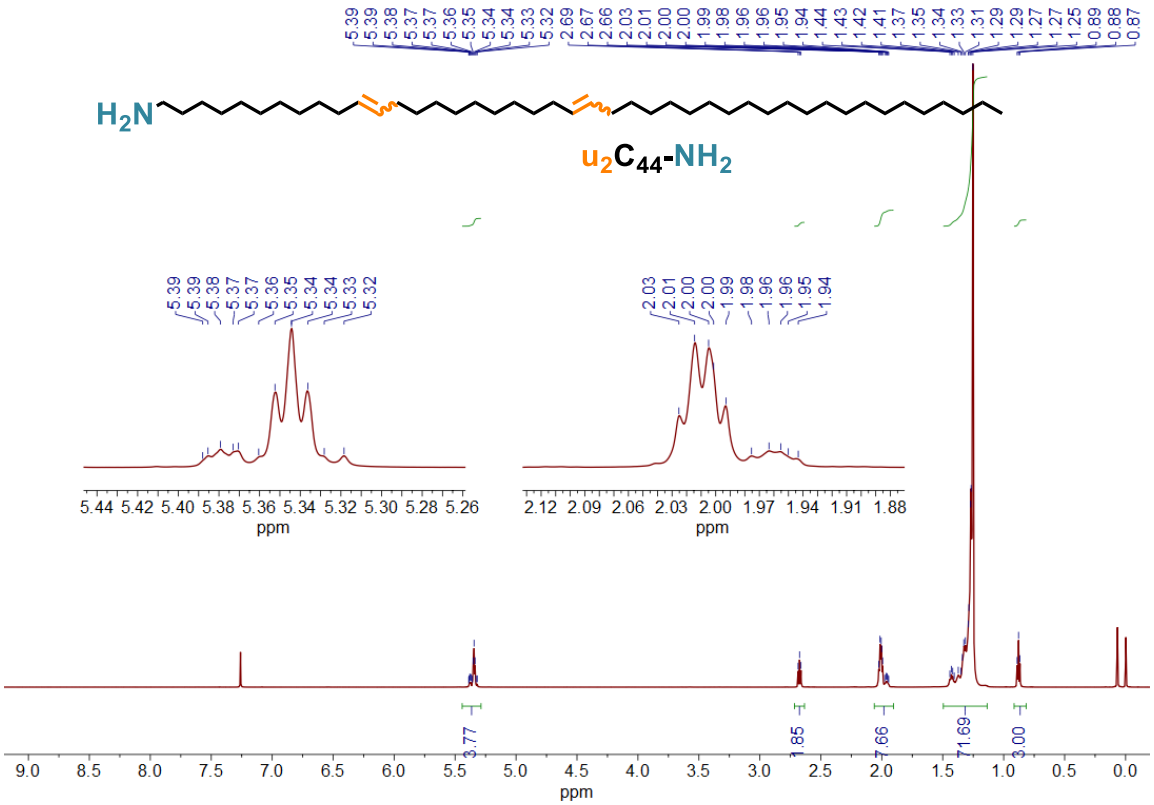

Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **$u_2C_{44}NH_2$.**

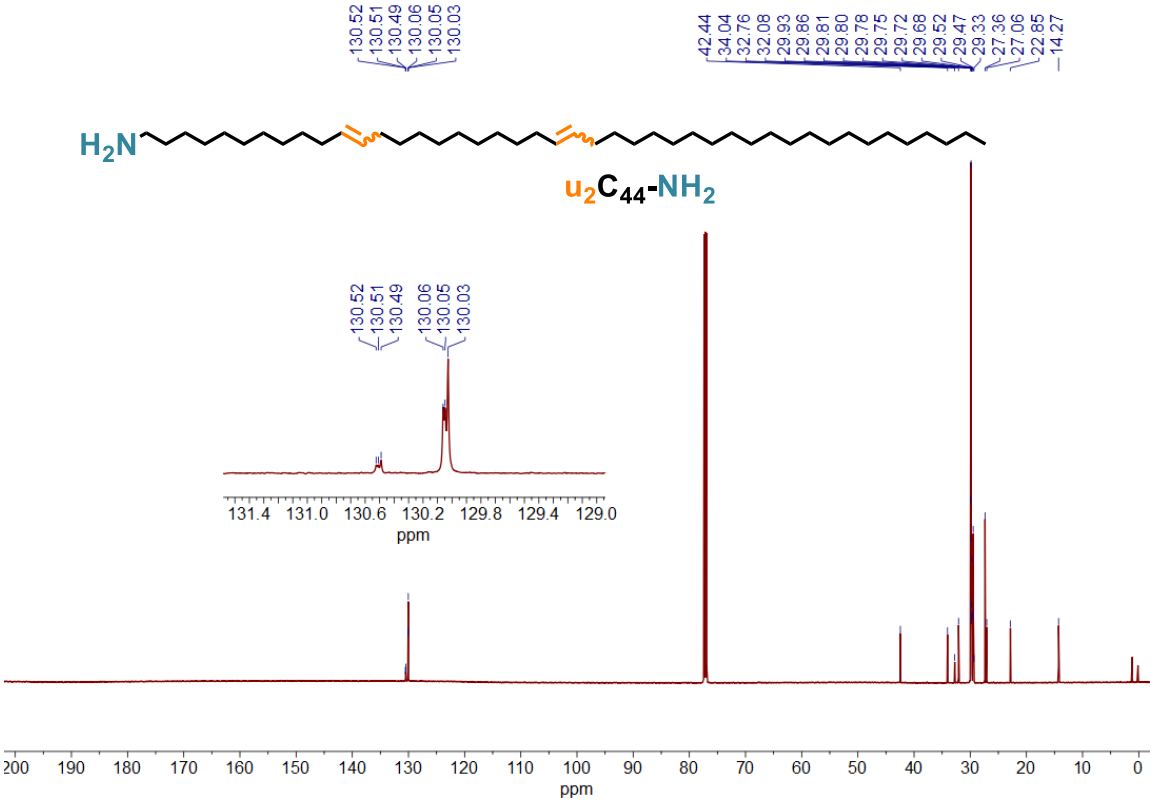

Figure S4. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **$u_2C_{44}NH_2$.**

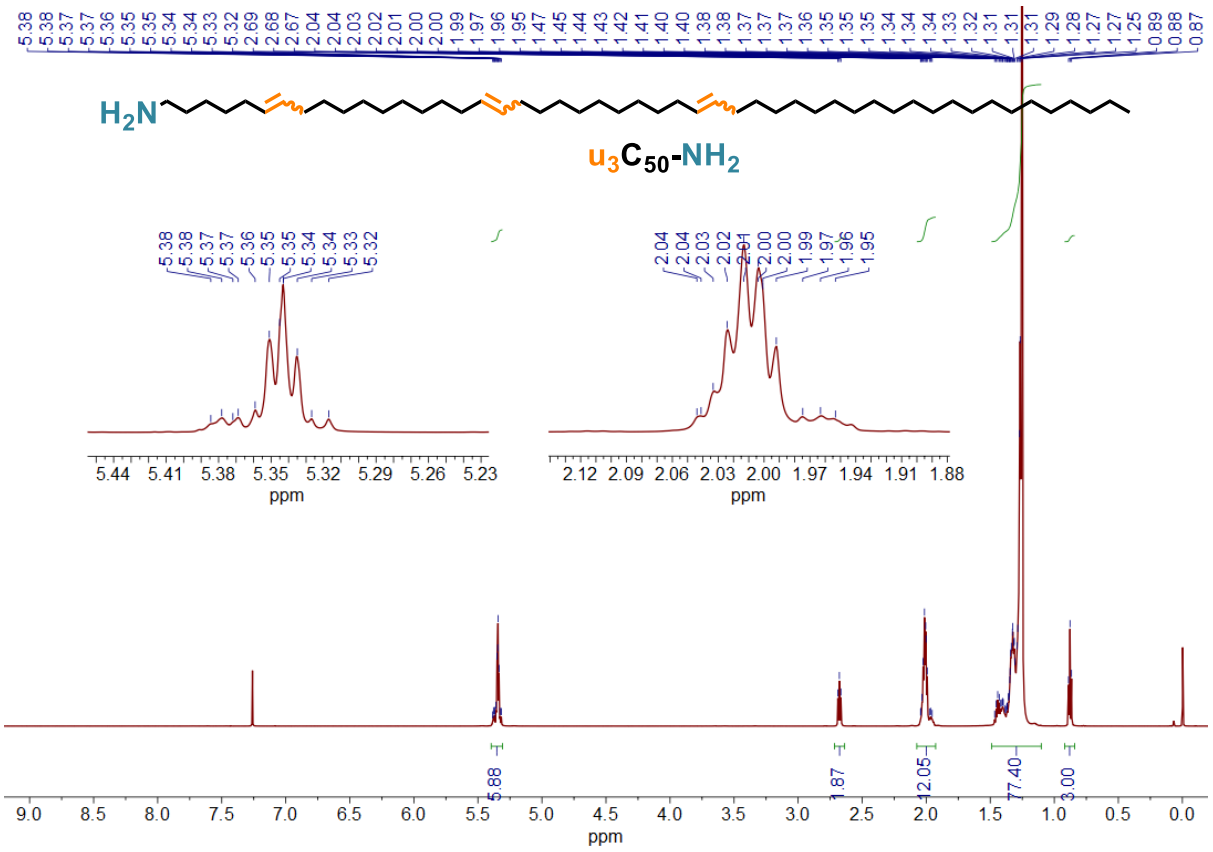

Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **$u_3C_{50}NH_2$.**

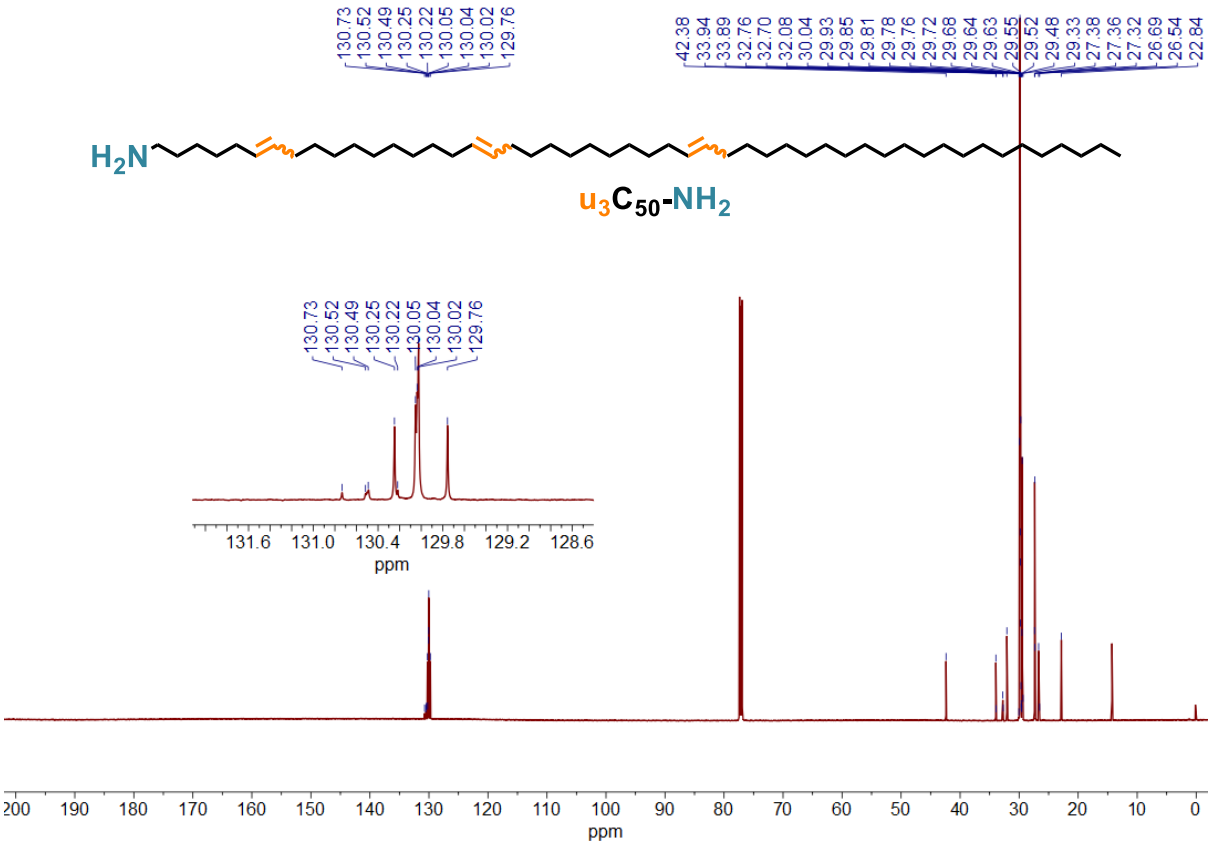

Figure S6. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **$u_3C_{50}NH_2$.**

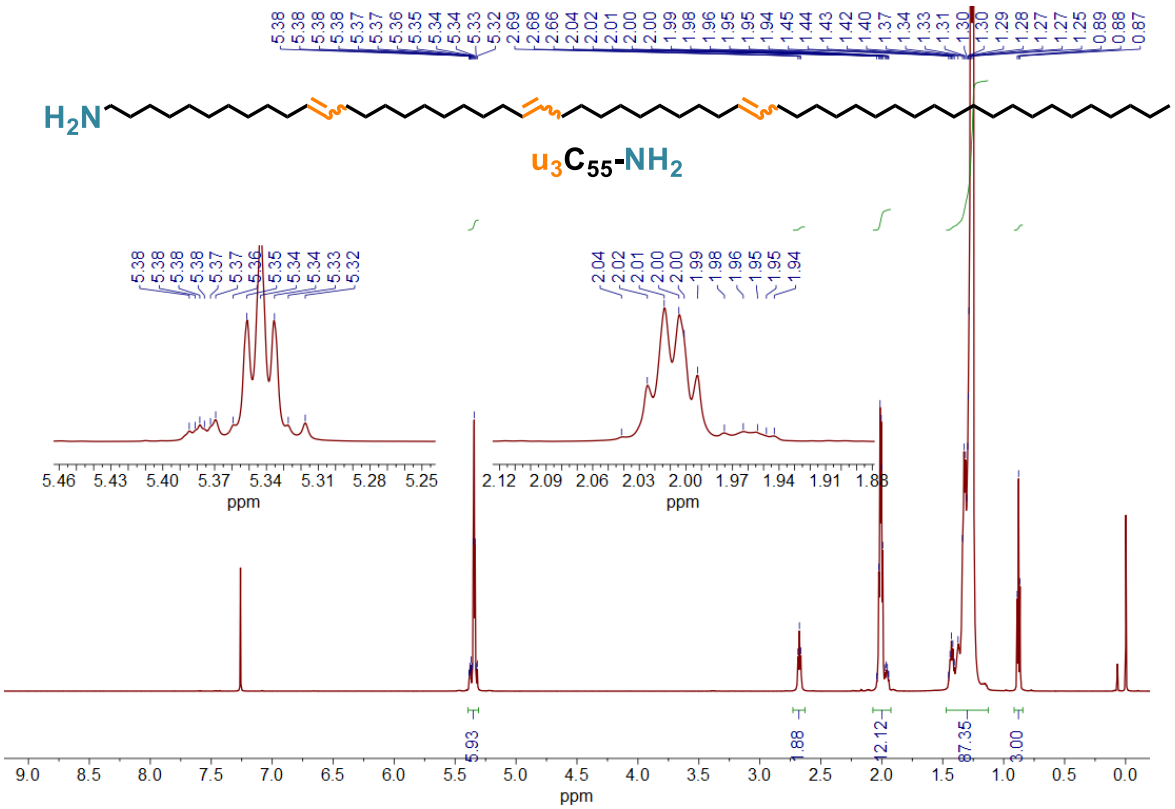

Figure S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **$u_3C_{55}NH_2$.**

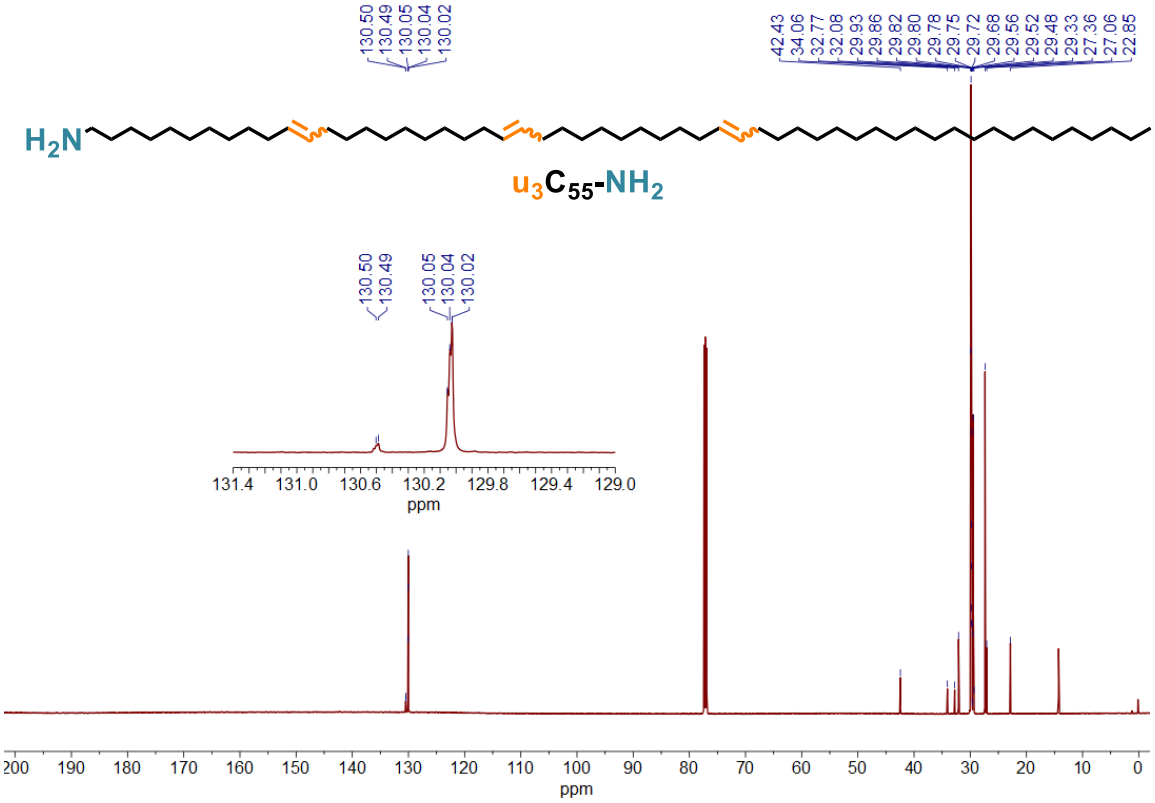

Figure S8. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **$u_3C_{55}NH_2$.**

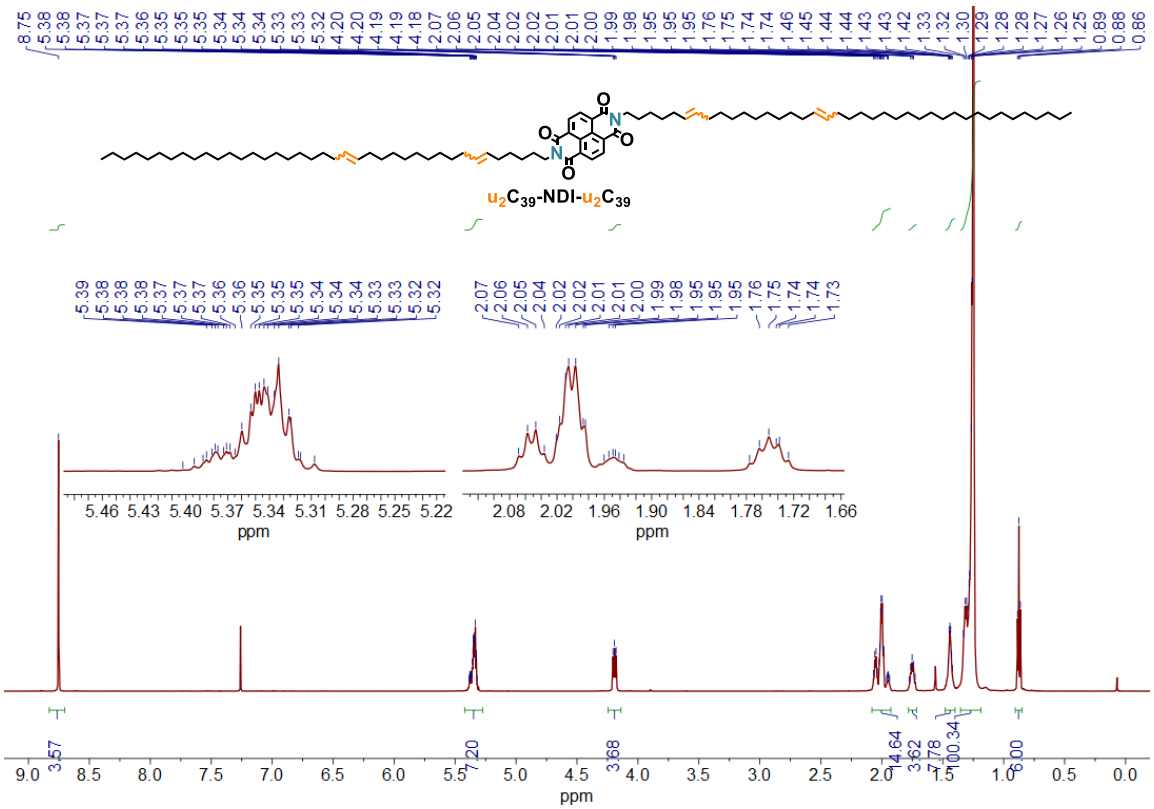

Figure S9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **u_2C_{39}-NDI-u_2C_{39}.**

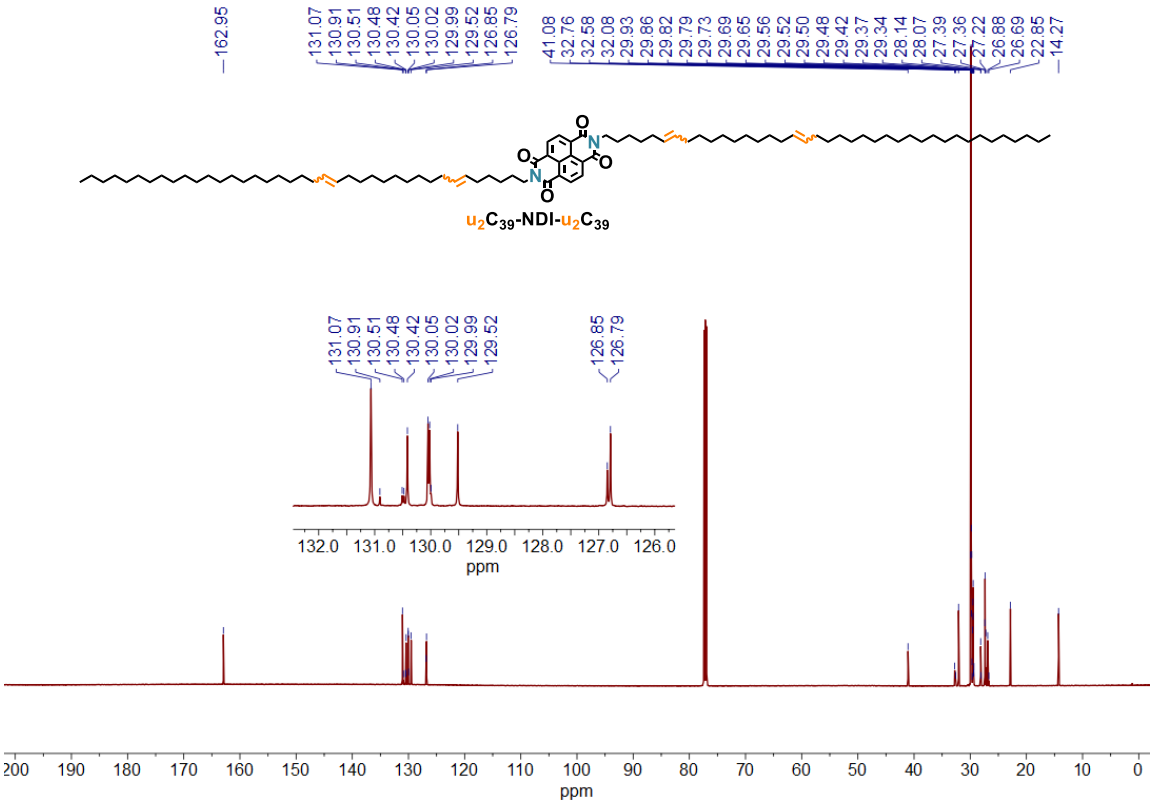

Figure S10. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **u_2C_{39}-NDI-u_2C_{39}.**

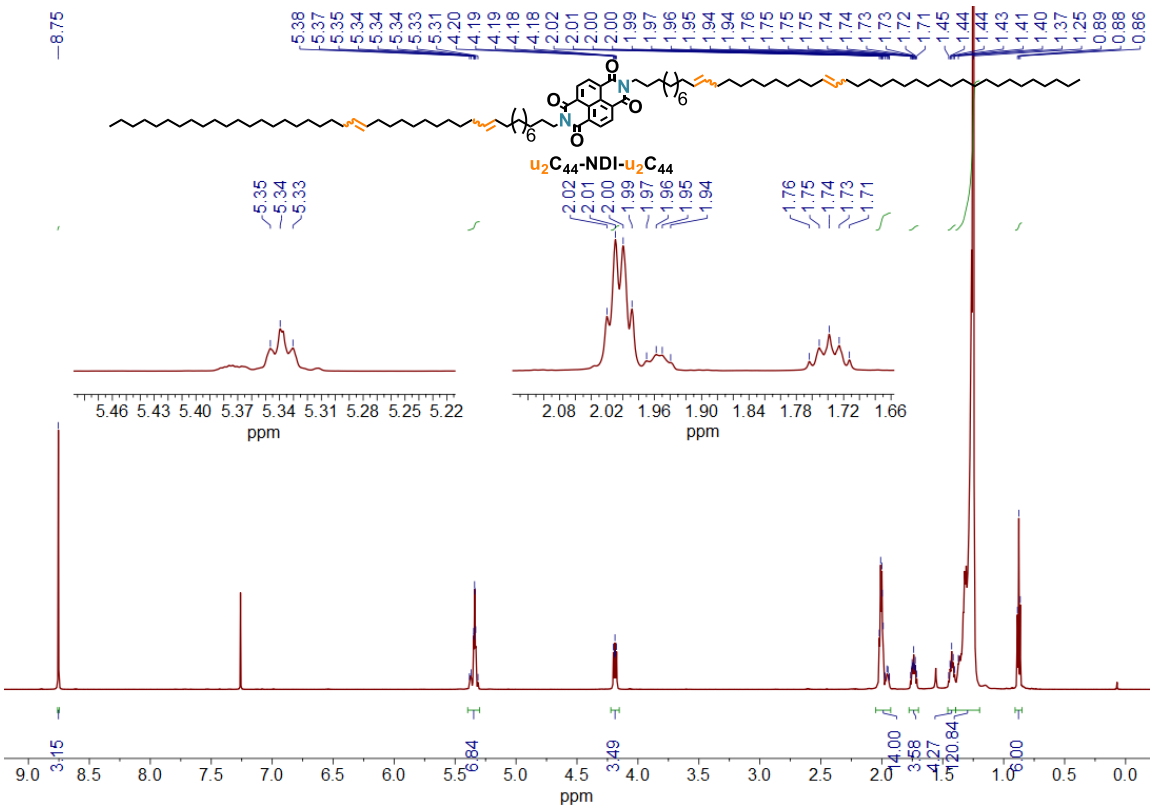

Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **u_2C_{44}-NDI-u_2C_{44}.**

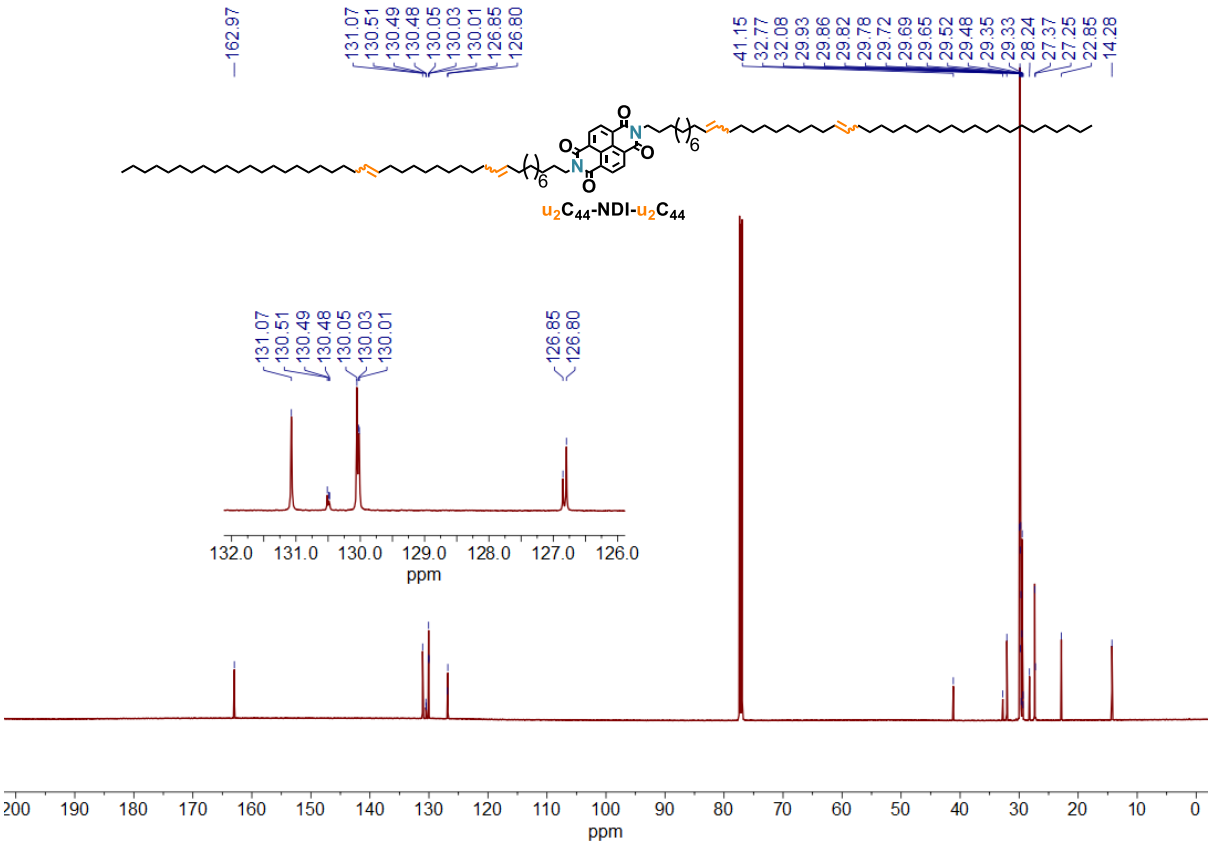

Figure S12. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **u_2C_{44}-NDI-u_2C_{44}.**

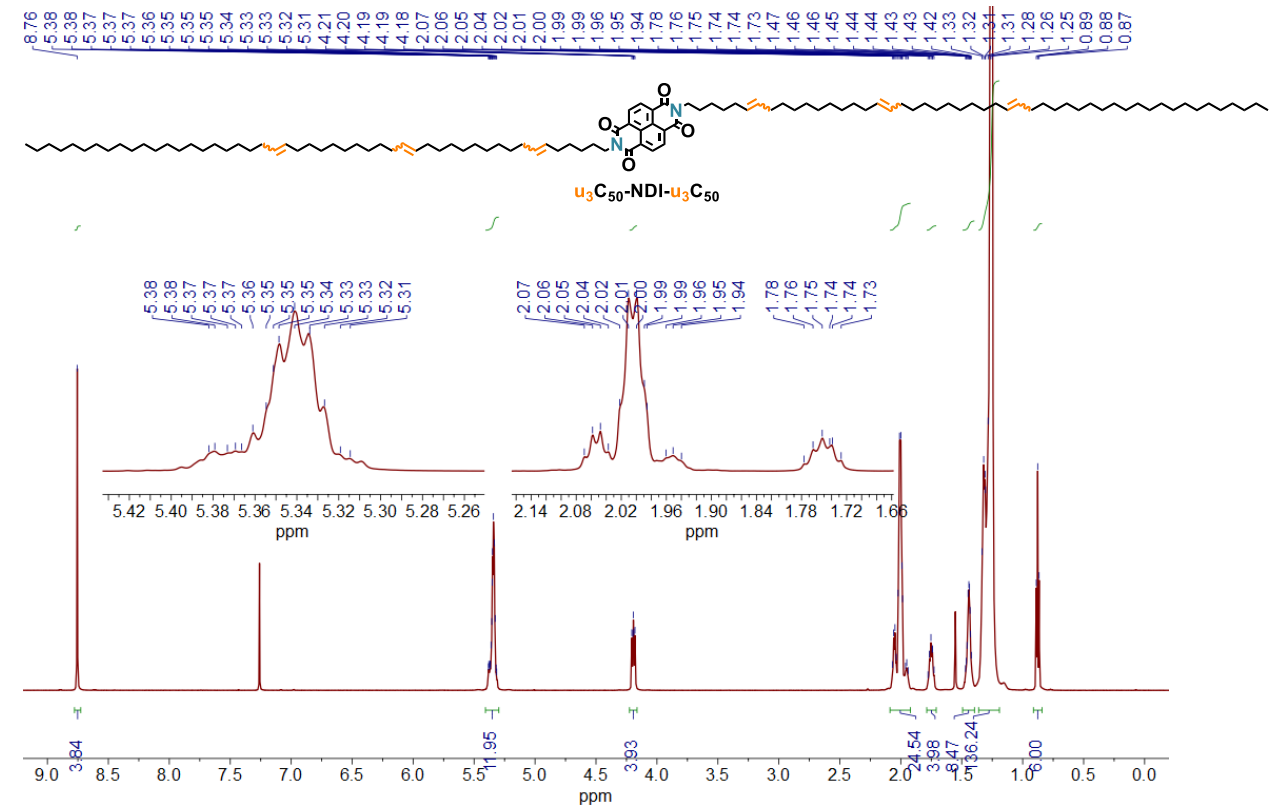

Figure S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **u$_3$C$_{50}$-NDI-u$_3$C$_{50}$.**

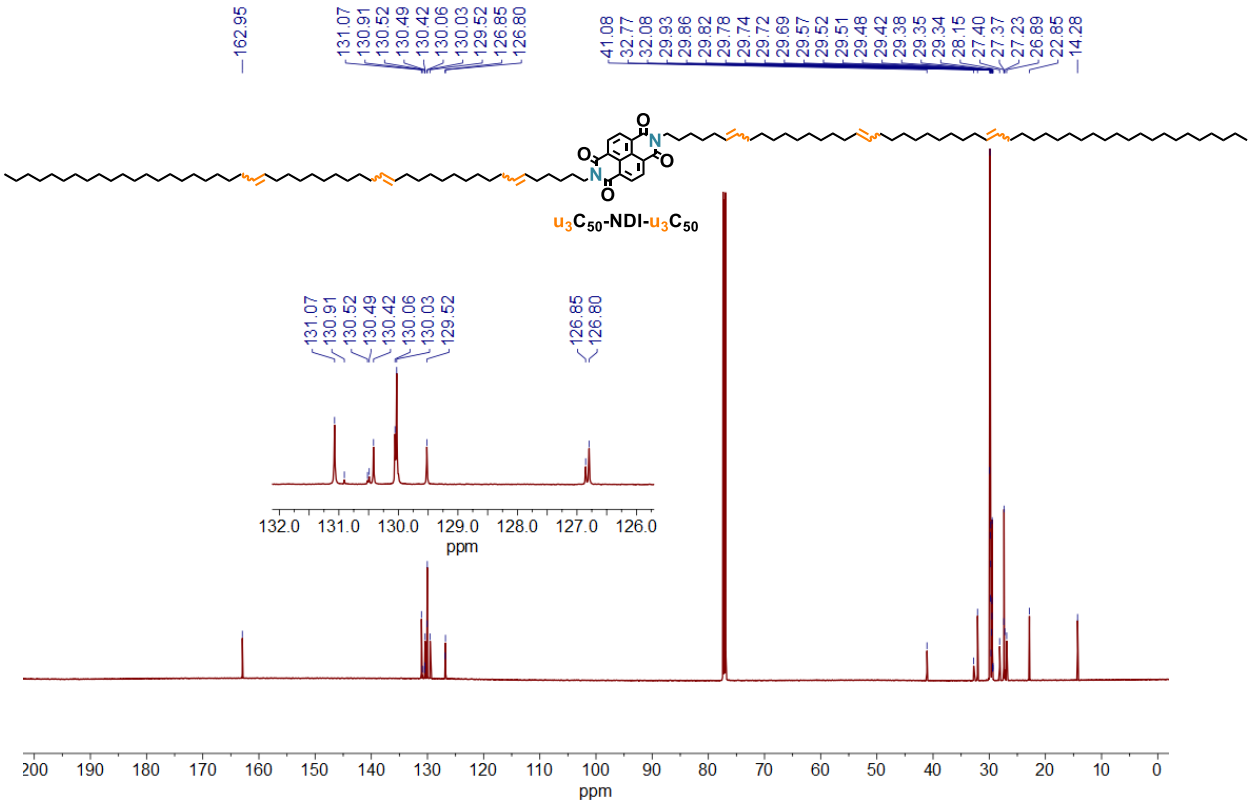

Figure S14. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **u$_3$C$_{50}$-NDI-u$_3$C$_{50}$.**

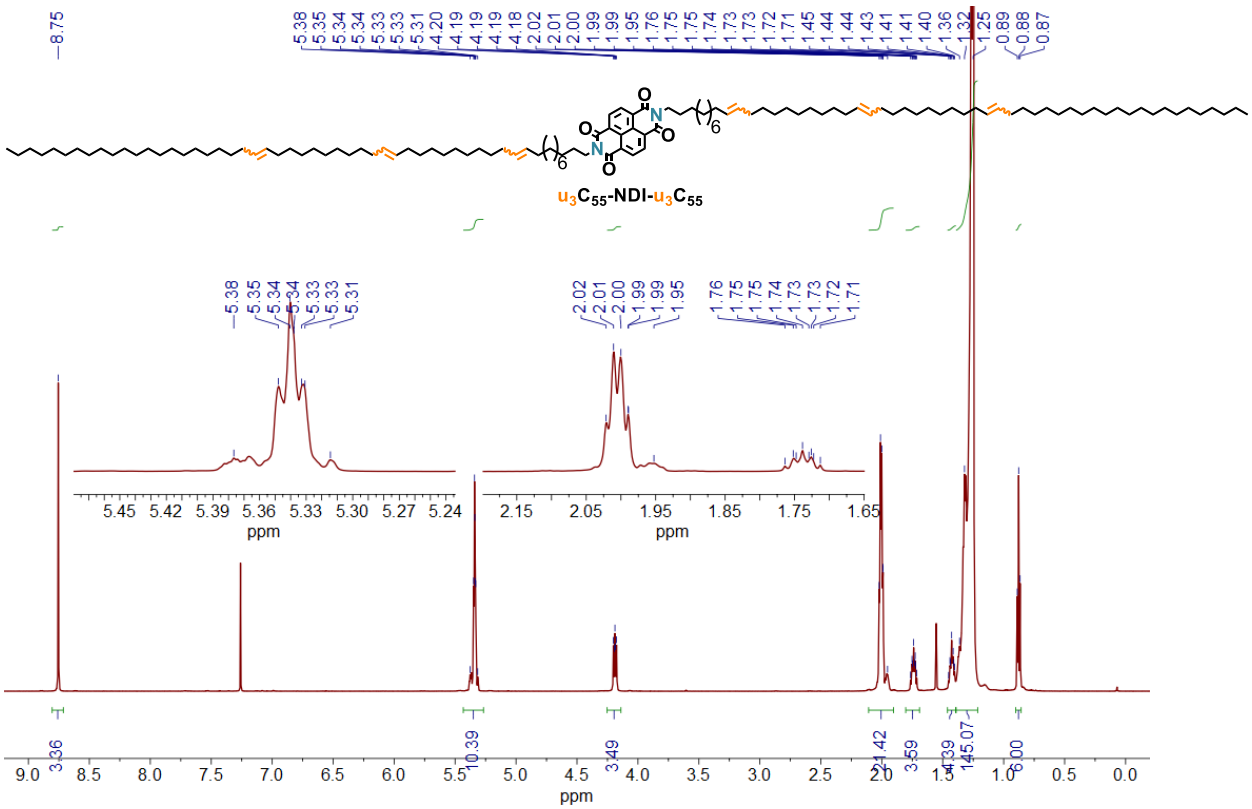

Figure S15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25 ºC) of **u_3C_{55}-NDI-u_3C_{55}.**

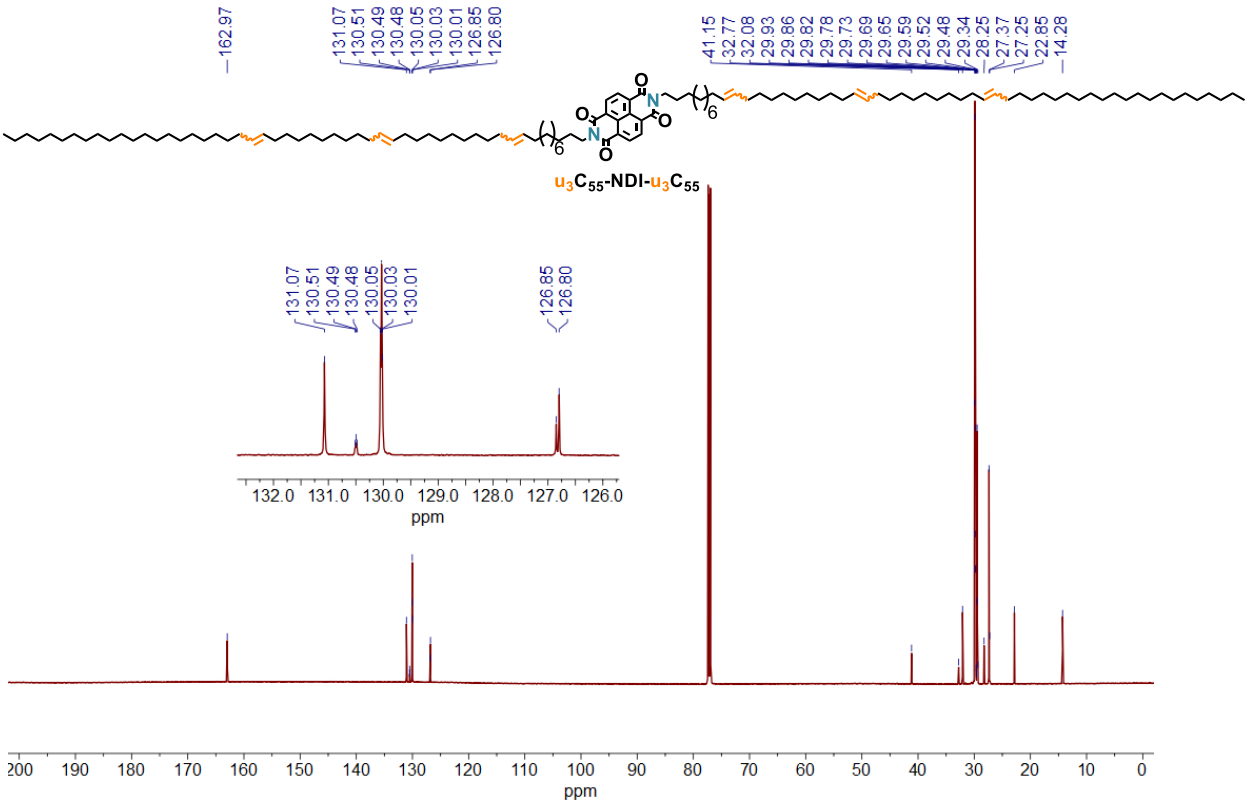

Figure S16. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 25 ºC) of **u_3C_{55}-NDI-u_3C_{55}.**

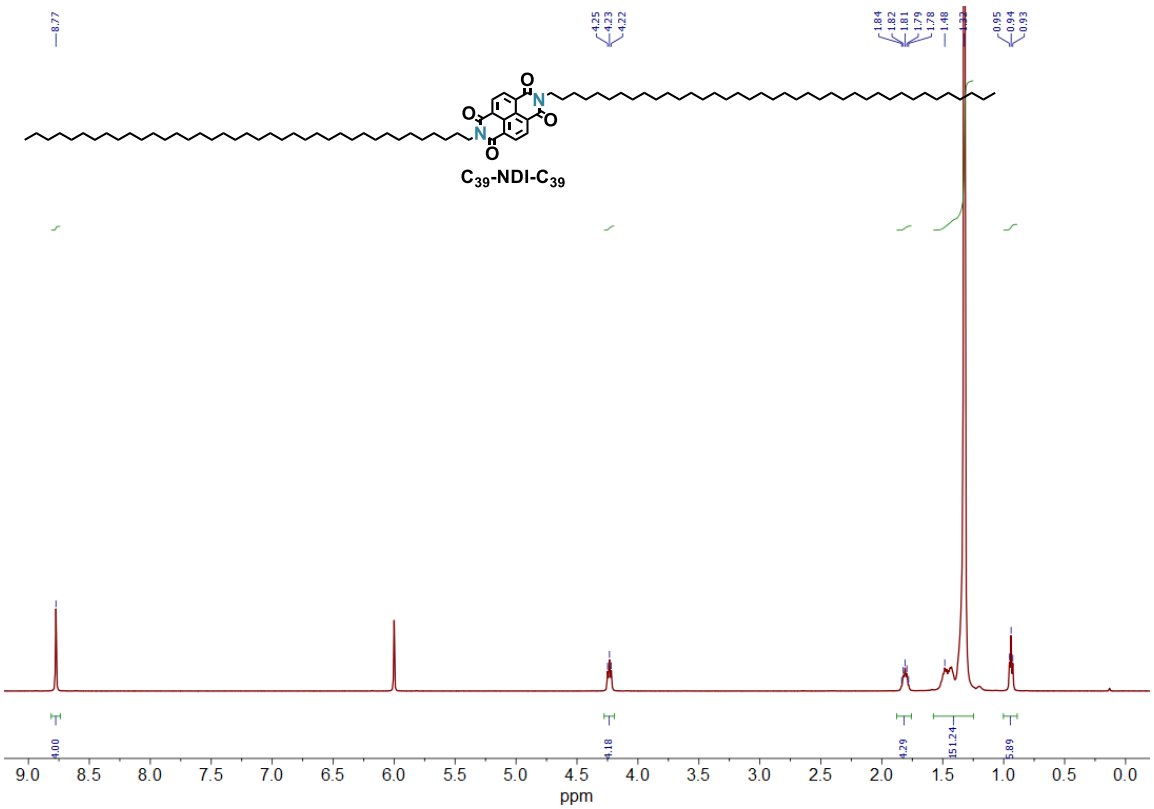

Figure S17. ^{1}H NMR spectrum (500 MHz, $Cl_2DCCDCl_2$, 85 ºC) of **C_{39}-NDI-C_{39}.**

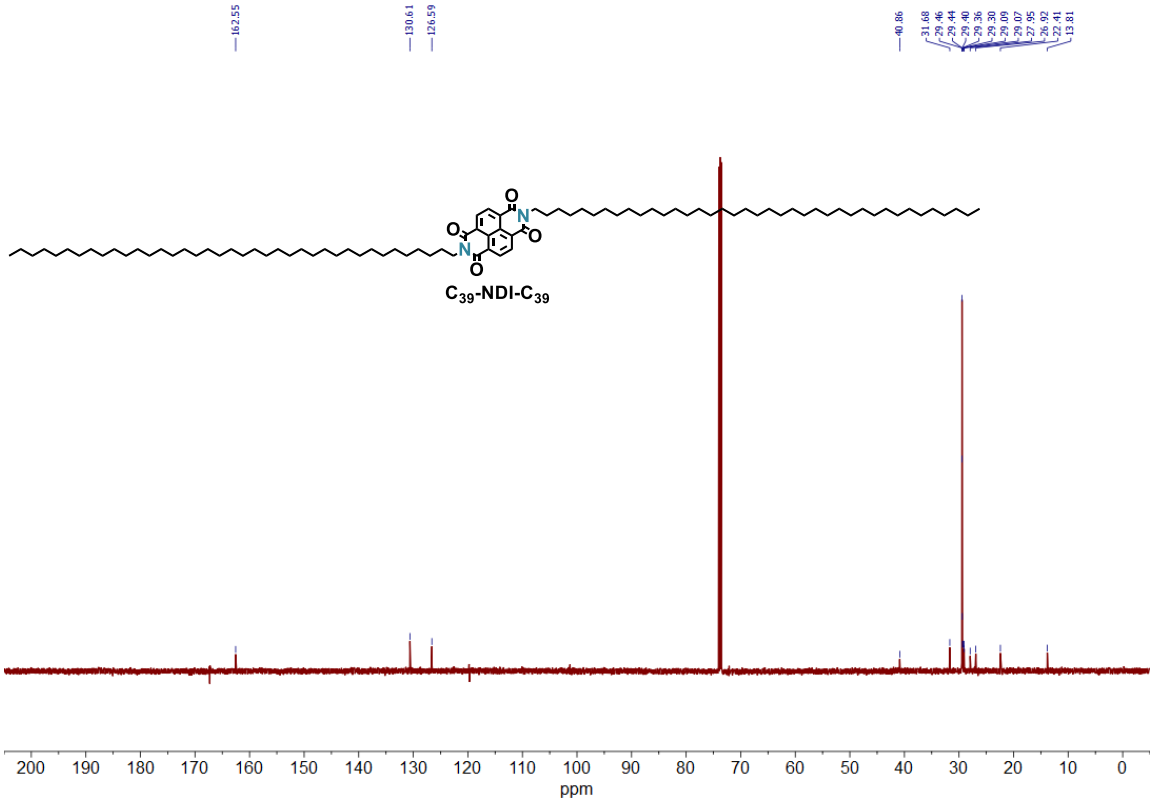

Figure S18. ^{13}C NMR spectrum (125 MHz, $Cl_2DCCDCl_2$, 85 ºC) of **C_{39}-NDI-C_{39}.**

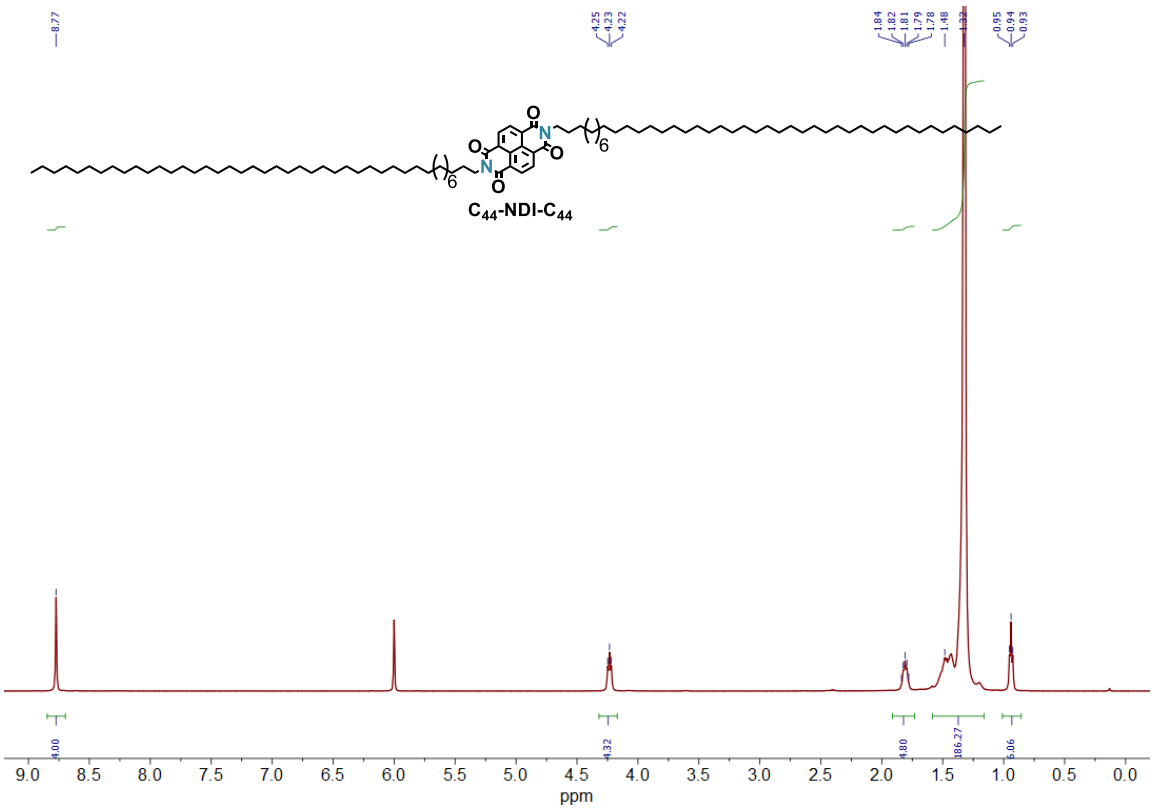

Figure S19. ^{1}H NMR spectrum (500 MHz, $Cl_2DCCDCl_2$, 85 ºC) of **C_{44}-NDI-C_{44}.**

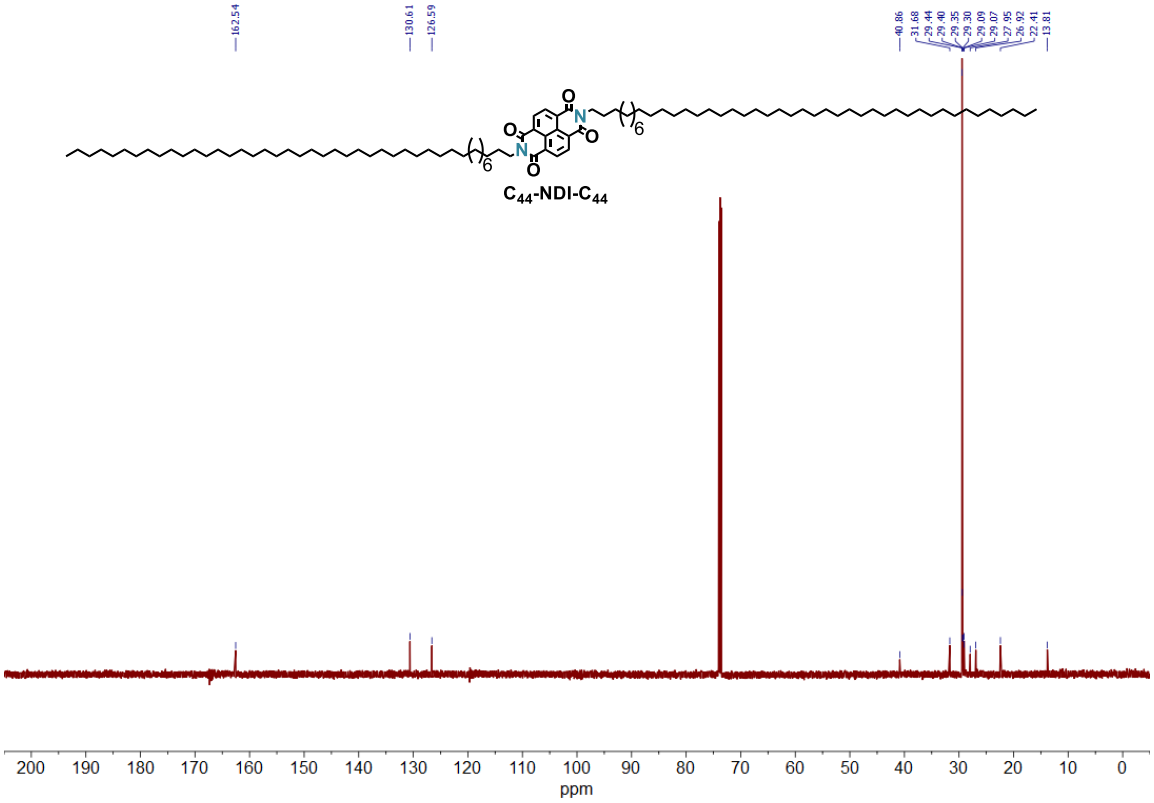

Figure S20. ^{13}C NMR spectrum (125 MHz, $Cl_2DCCDCl_2$, 85 ºC) of **C_{44}-NDI-C_{44}.**

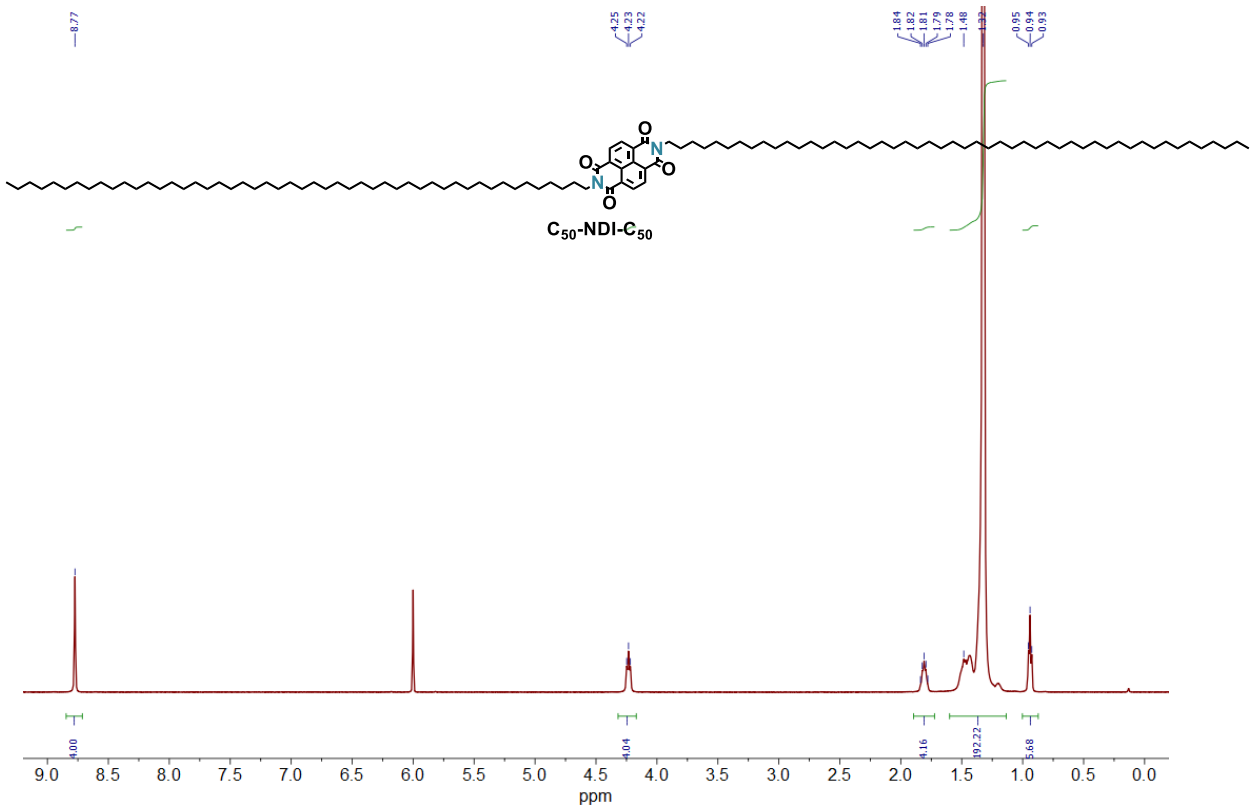

Figure S21. ^{1}H NMR spectrum (500 MHz, $Cl_2DCCDCl_2$, 85 ºC) of **C_{50}-NDI-C_{50}.**

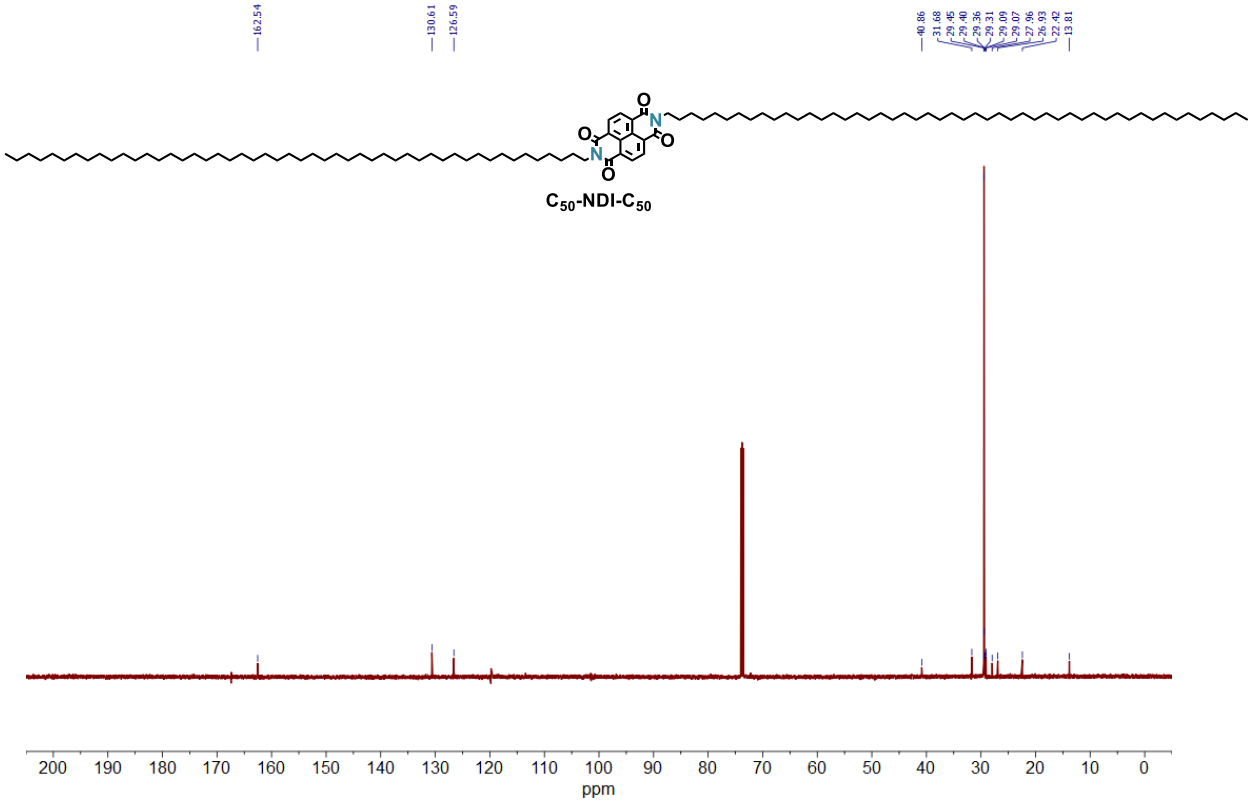

Figure S22. ^{13}C NMR spectrum (125 MHz, $Cl_2DCCDCl_2$, 85 ºC) of **C_{50}-NDI-C_{50}.**

FT-IR spectra

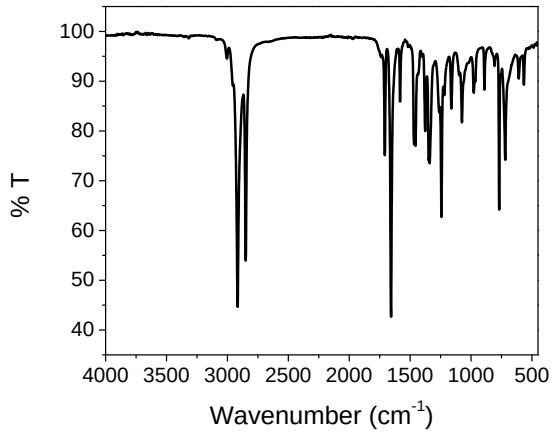

Figure S23. FT-IR spectrum of **u$_2$C$_{39}$-NDI-u$_2$C$_{39}$**.

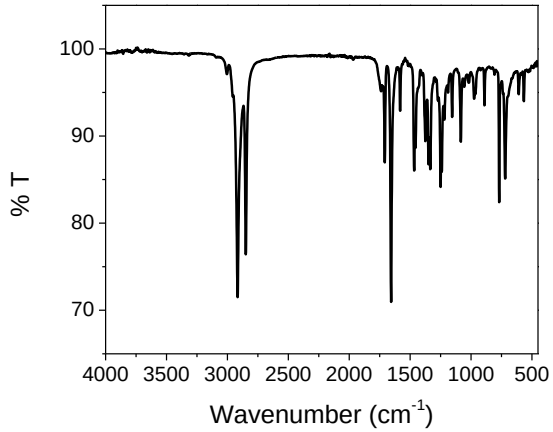

Figure S24. FT-IR spectrum of **u$_2$C$_{44}$-NDI-u$_2$C$_{44}$**.

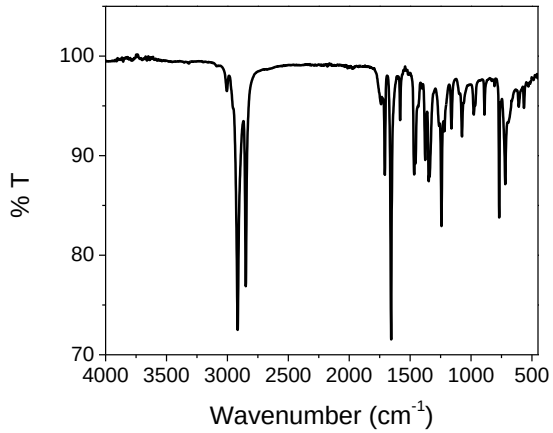

Figure S25. FT-IR spectrum of **u$_3$C$_{50}$-NDI-u$_3$C$_{50}$**.

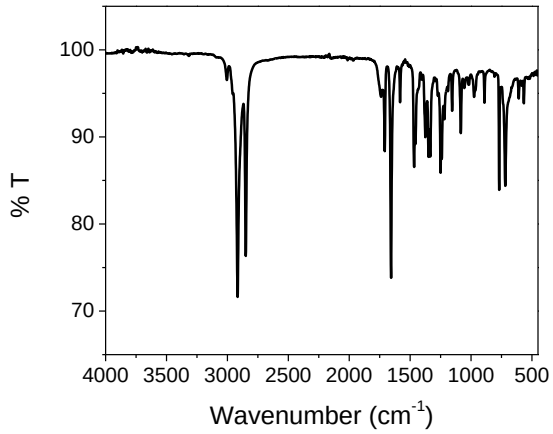

Figure S26. FT-IR spectrum of **u$_3$C$_{55}$-NDI-u$_3$C$_{55}$.**

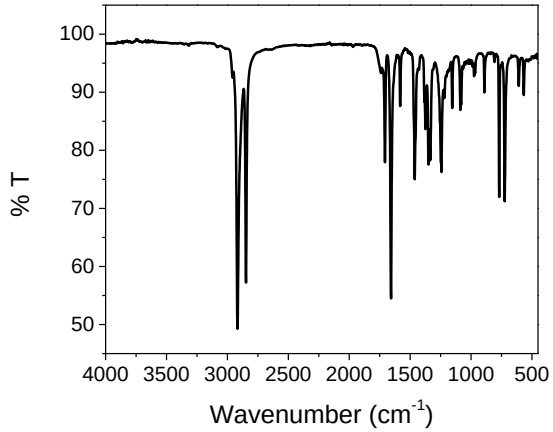

Figure S27. FT-IR spectrum of **C$_{39}$-NDI-C$_{39}$.**

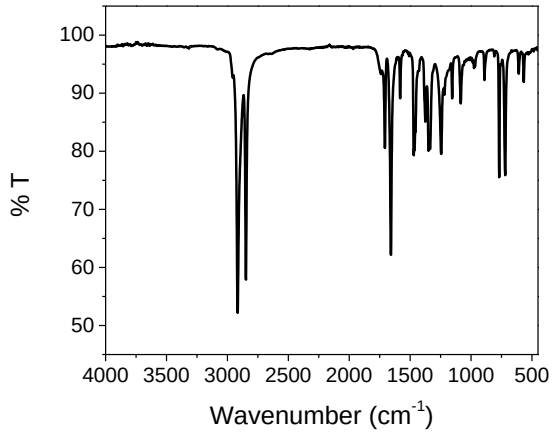

Figure S28. FT-IR spectrum of **C$_{44}$-NDI-C$_{44}$.**

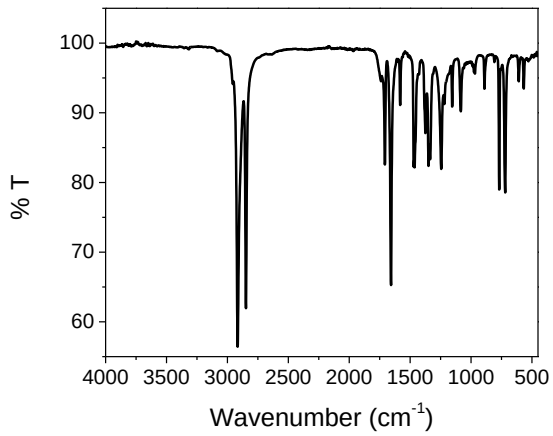

Figure S29. FT-IR spectrum of **C_{50}-NDI-C_{50}**.

DSC traces

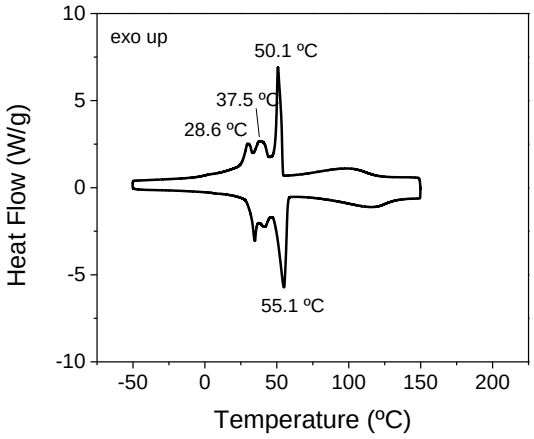

Figure S30. DSC trace of **u$_2$C$_{39}$-NH$_2$** (exo up, heating/cooling rate 5 ºC/min).

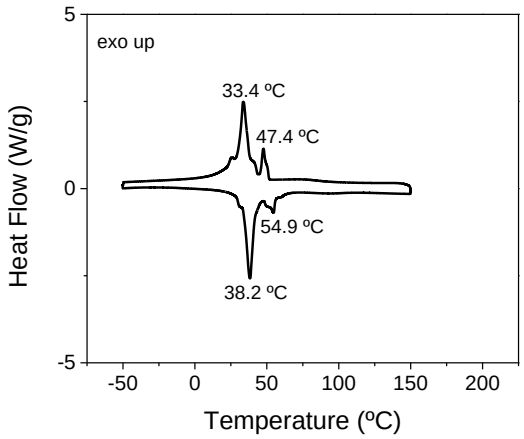

Figure S31. DSC trace of **u$_2$C$_{44}$-NH$_2$** (exo up, heating/cooling rate 5 ºC/min).

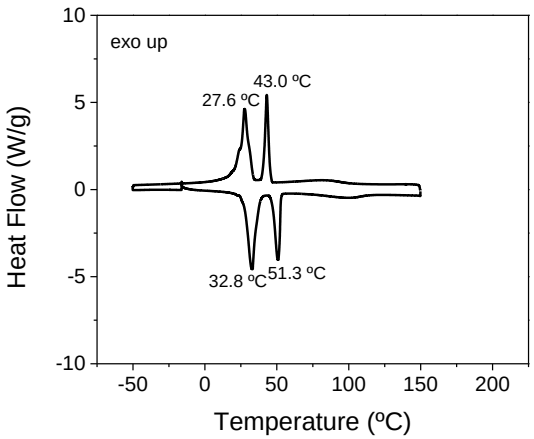

Figure S32. DSC trace of **u$_3$C$_{50}$-NH$_2$** (exo up, heating/cooling rate 5 ºC/min).

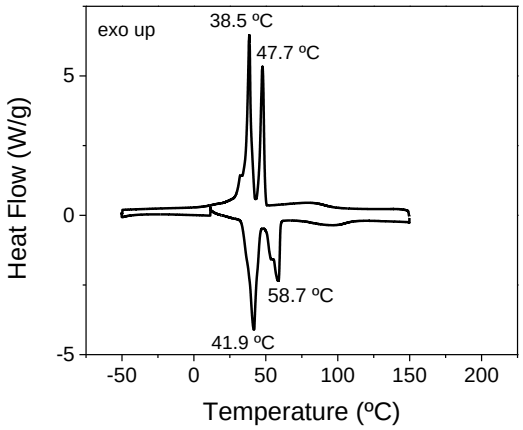

Figure S33. DSC trace of **u$_3$C$_{55}$-NH$_2$** (exo up, heating/cooling rate 5 ºC/min).

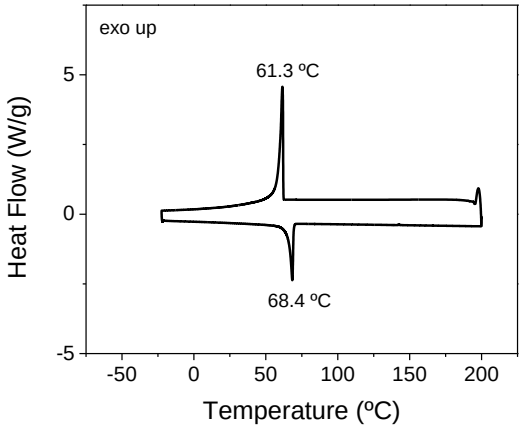

Figure S34. DSC trace of **u$_2$C$_{39}$-NDI-u$_2$C$_{39}$** (exo up, heating/cooling rate 5 ºC/min).

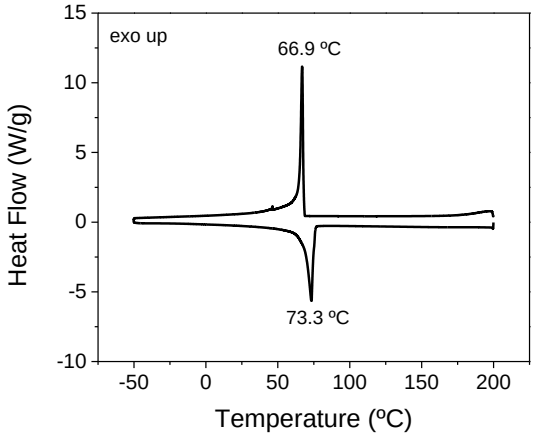

Figure S35. DSC trace of **u$_2$C$_{44}$-NDI-u$_2$C$_{44}$** (exo up, heating/cooling rate 5 ºC/min).

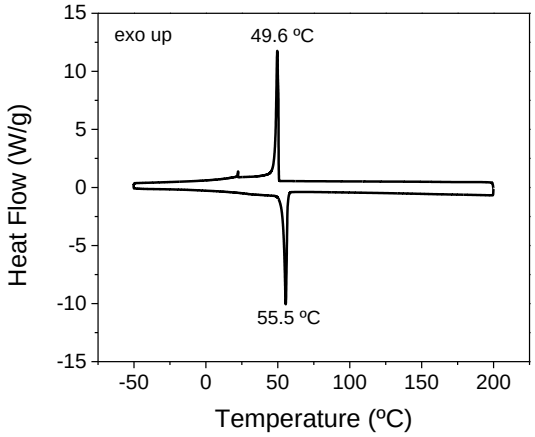

Figure S36. DSC trace of **u$_3$C$_{50}$-NDI-u$_3$C$_{50}$** (exo up, heating/cooling rate 5 ºC/min).

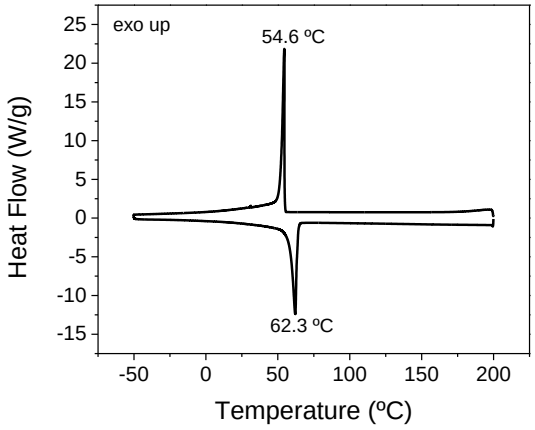

Figure S37. DSC trace of **u$_3$C$_{55}$-NDI-**u$_3$C$_{55}$ (exo up, heating/cooling rate 5 ºC/min).

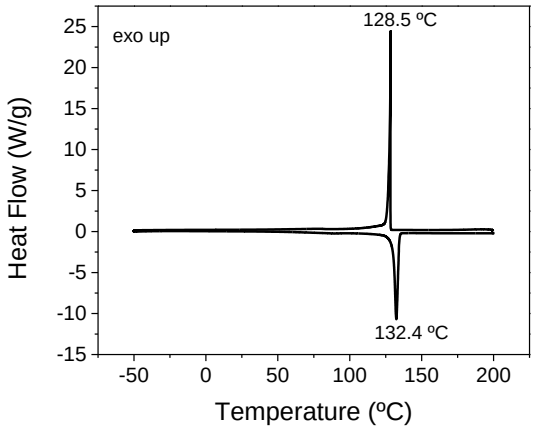

Figure S38. DSC trace of **C$_{39}$-NDI-C$_{39}$** (exo up, heating/cooling rate 5 ºC/min).

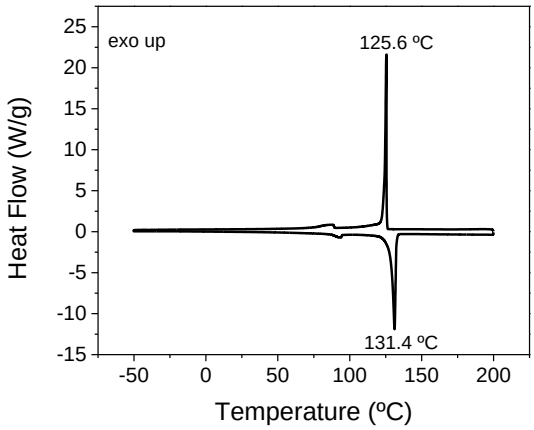

Figure S39. DSC trace of **C_{44}-NDI-C_{44}** (exo up, heating/cooling rate 5 ºC/min).

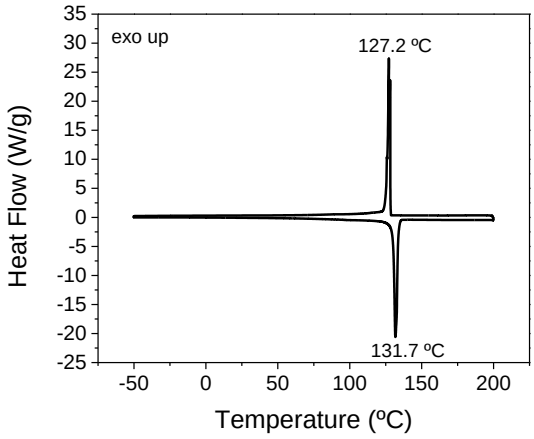

Figure S40. DSC trace of **C_{50}-NDI-C_{50}** (exo up, heating/cooling rate 5 ºC/min).

UV-vis spectrum of C_{44}-NDI-C_{44} in 1-PO

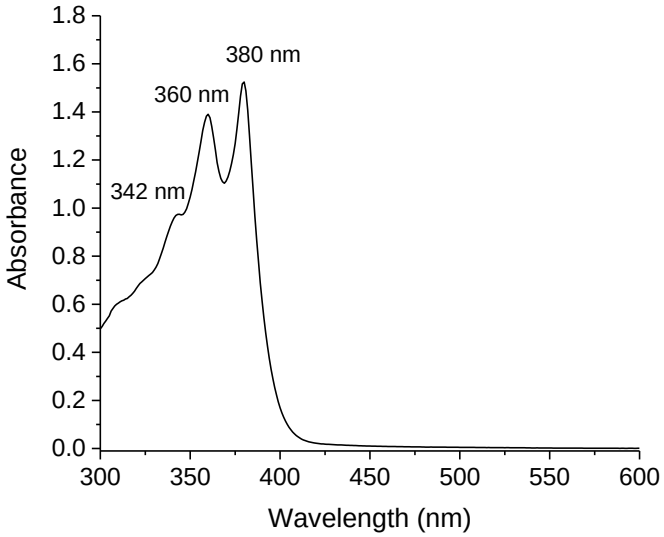

Figure S41. UV-Vis spectrum of **C_{44}-NDI-C_{44}** in 1-PO (0.40 mg/mL) measured after heating the sample at 100 ºC and cooling down to room temperature.

Additional STM images

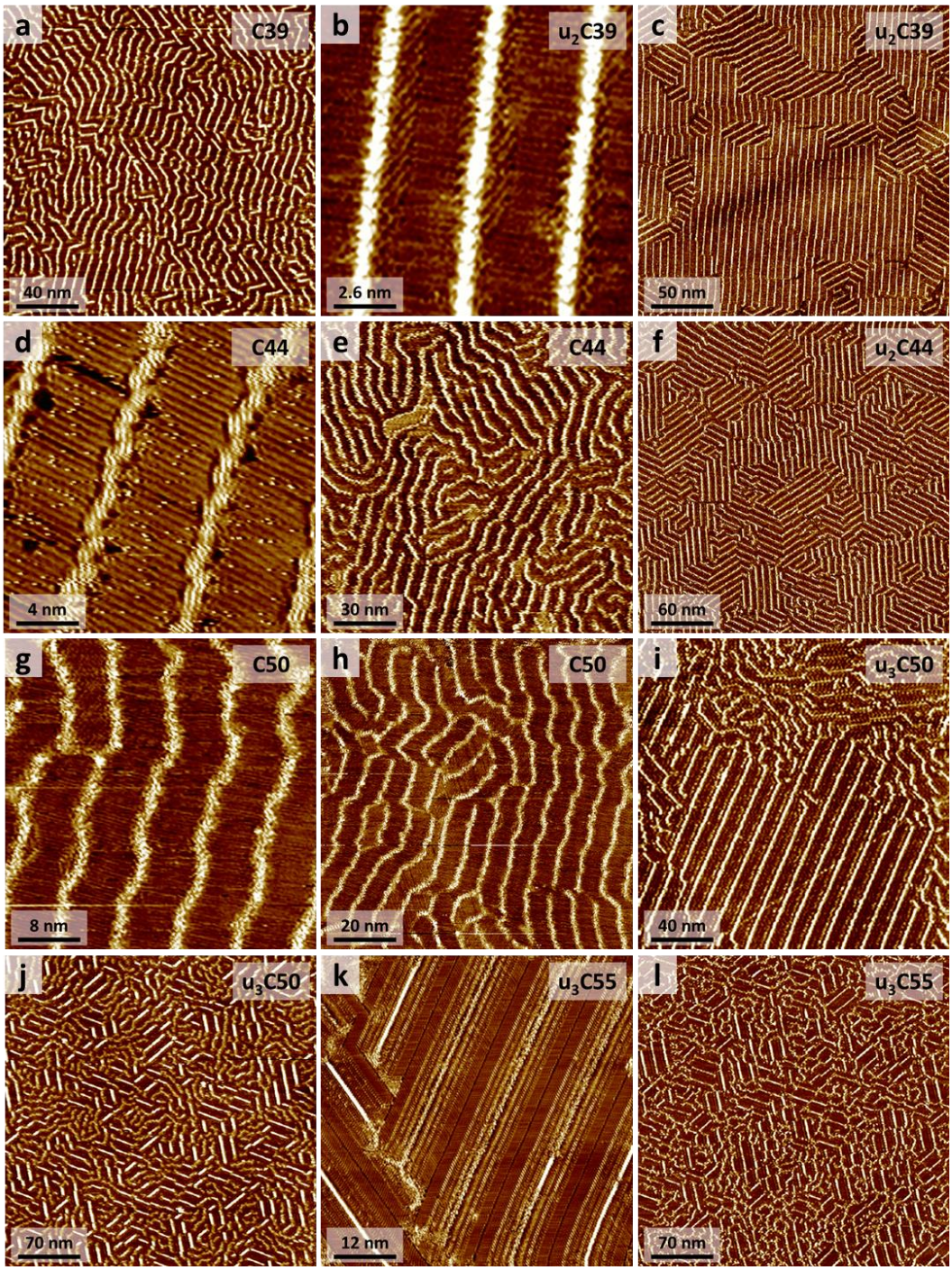

Figure S42. STM topography images of unsaturated/saturated **C_n-NDI-C_n** at the 1-PO/HOPG interface. a) V_{tip} = 1 V, I_{set} = 50 pA; b) V_{tip} = 1 V, I_{set} = 20 pA; c) V_{tip} = 1 V, I_{set} = 50 pA; d) V_{tip} = 1.3 V, I_{set} = 100 pA; e)V_{tip} = 1 V, I_{set} = 50 pA; f) V_{tip} = 1 V, I_{set} = 50 pA; g) V_{tip} = 1 V, I_{set} = 20 pA; h) V_{tip} = 1 V, I_{set} = 20 pA; i) V_{tip} = 1 V, I_{set} = 80 pA; j) V_{tip} = 1 V, I_{set} = 80 pA; k) V_{tip} = 1.4 V, I_{set} = 500 pA and l) V_{tip} = 1.1 V, I_{set} = 100 pA**.**

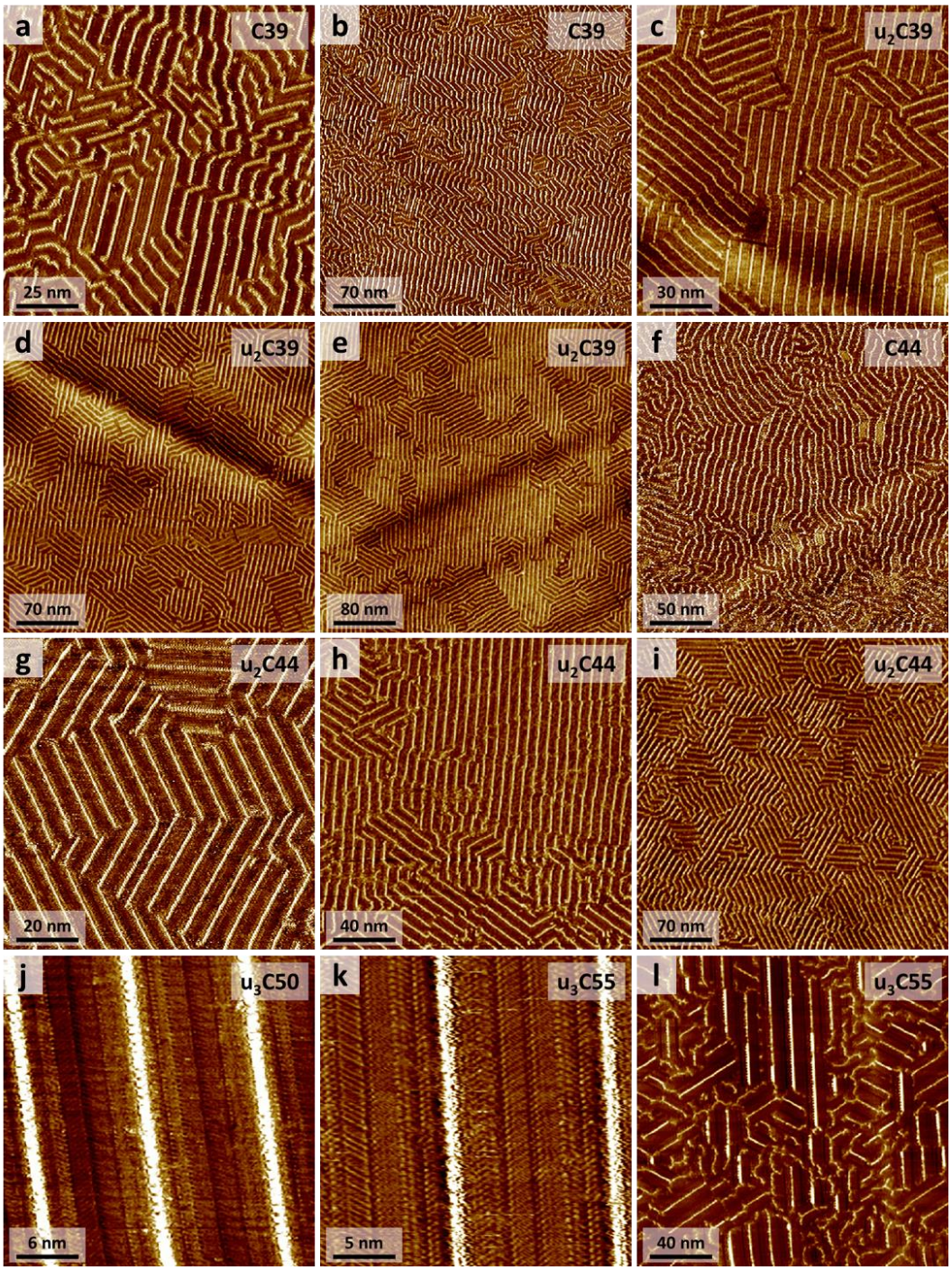

Figure S43. STM topography images of unsaturated/saturated **C_n-NDI-C_n** at the 1-PO/HOPG interface. a) Vtip = 1 V, Iset = 100 pA; b) Vtip = 1 V, Iset = 100 pA; c) Vtip = 1 V, Iset = 60 pA; d) Vtip = 1 V, Iset = 60 pA; e)Vtip = 1 V, Iset = 50 pA; f) Vtip = 1 V, Iset = 100 pA; g) Vtip = 1 V, Iset = 100 pA; h) Vtip = 1 V, Iset = 100 pA; i) Vtip = 1 V, Iset = 100 pA; j) Vtip = 1 V, Iset = 60 pA; k) Vtip = 1.3 V, Iset = 25 pA and l) Vtip = 1 V, Iset = 100 pA.

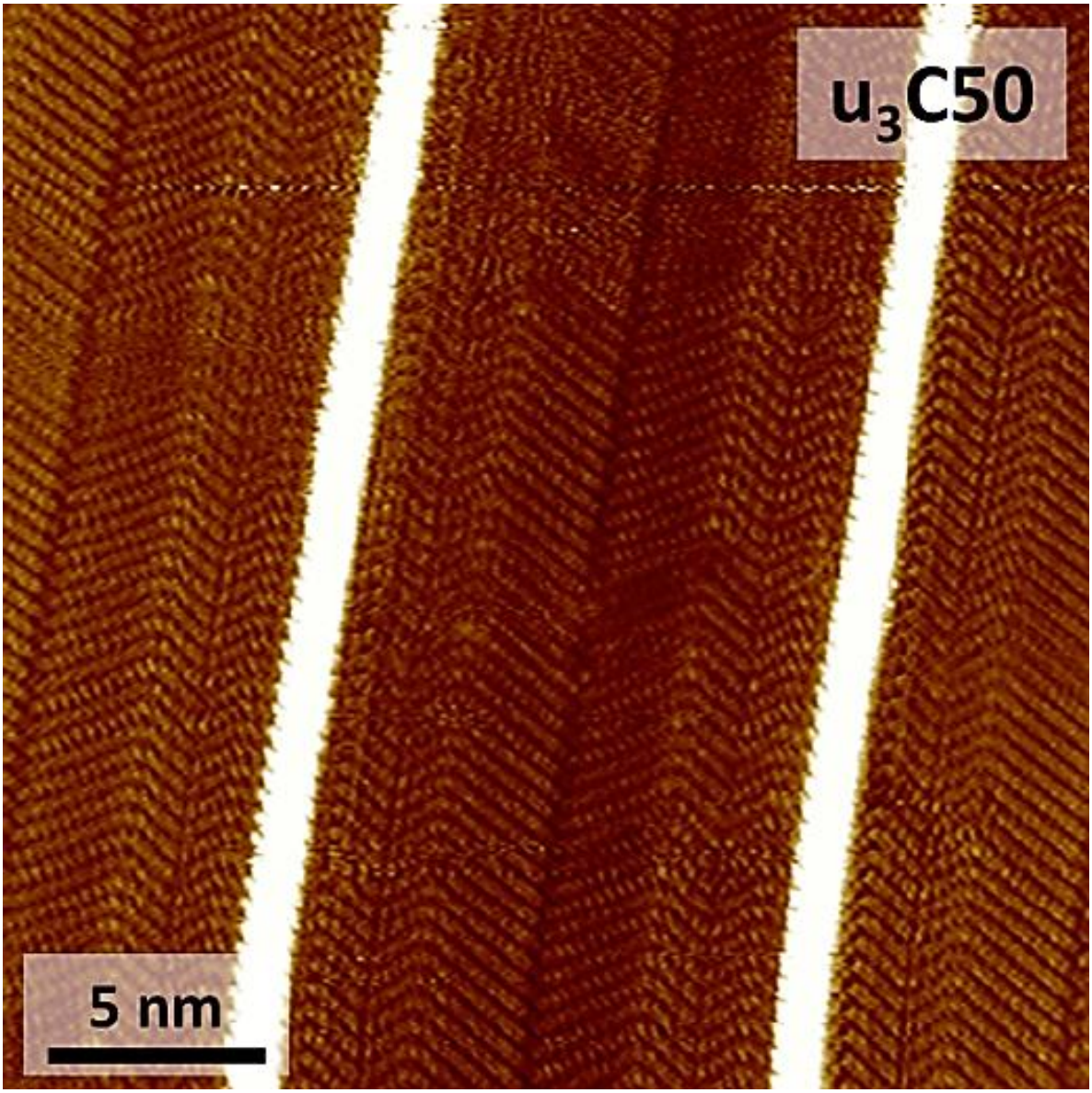

Figure S44. Enlarged STM image of **u$_3$C$_{50}$-NDI-u$_3$C$_{50}$** (25 nm × 25 nm, V_{tip} = 0.9 V, I_{set} = 40 pA).

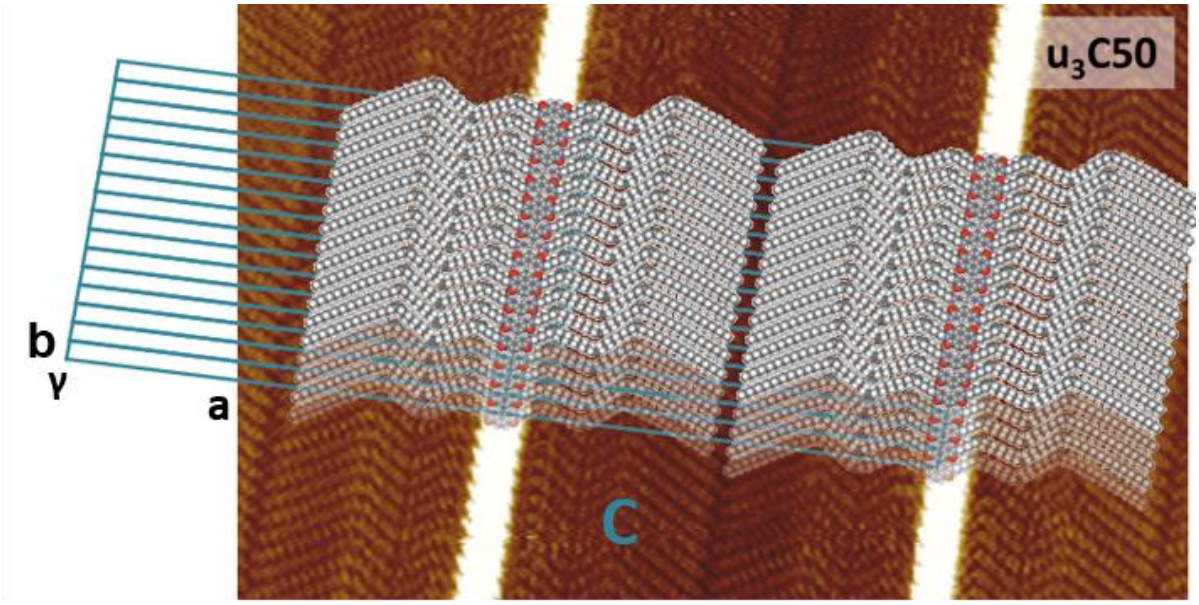

Figure S45. Qualitative molecular model showing the organization of **u3C50-NDI-u3C50** in lamellar phase C.

References

(S1) van Genabeek, B.; De Waal, B. F. M.; Palmans, A. R. A.; Meijer, E. W. Discrete Oligodimethylsiloxane–Oligomethylene Di- and Triblock Co-Oligomers: Synthesis, Self-Assembly and Molecular Organisation. *Polym. Chem* **2018**, *9*, 2746–2758.

(S2) Berrocal, J. A.; Heideman, G. H.; De Waal, B. F. M.; Enache, M.; Havenith, R. W. A.; Meijer, E. W.; Feringa, B. L. Engineering Long-Range Order in Supramolecular Assemblies on Surfaces: The Paramount Role of Internal Double Bonds in Discrete Long-Chain Naphthalenediimides. *J. Am. Chem. Soc.* **2020**, *142*, 4070–4078.