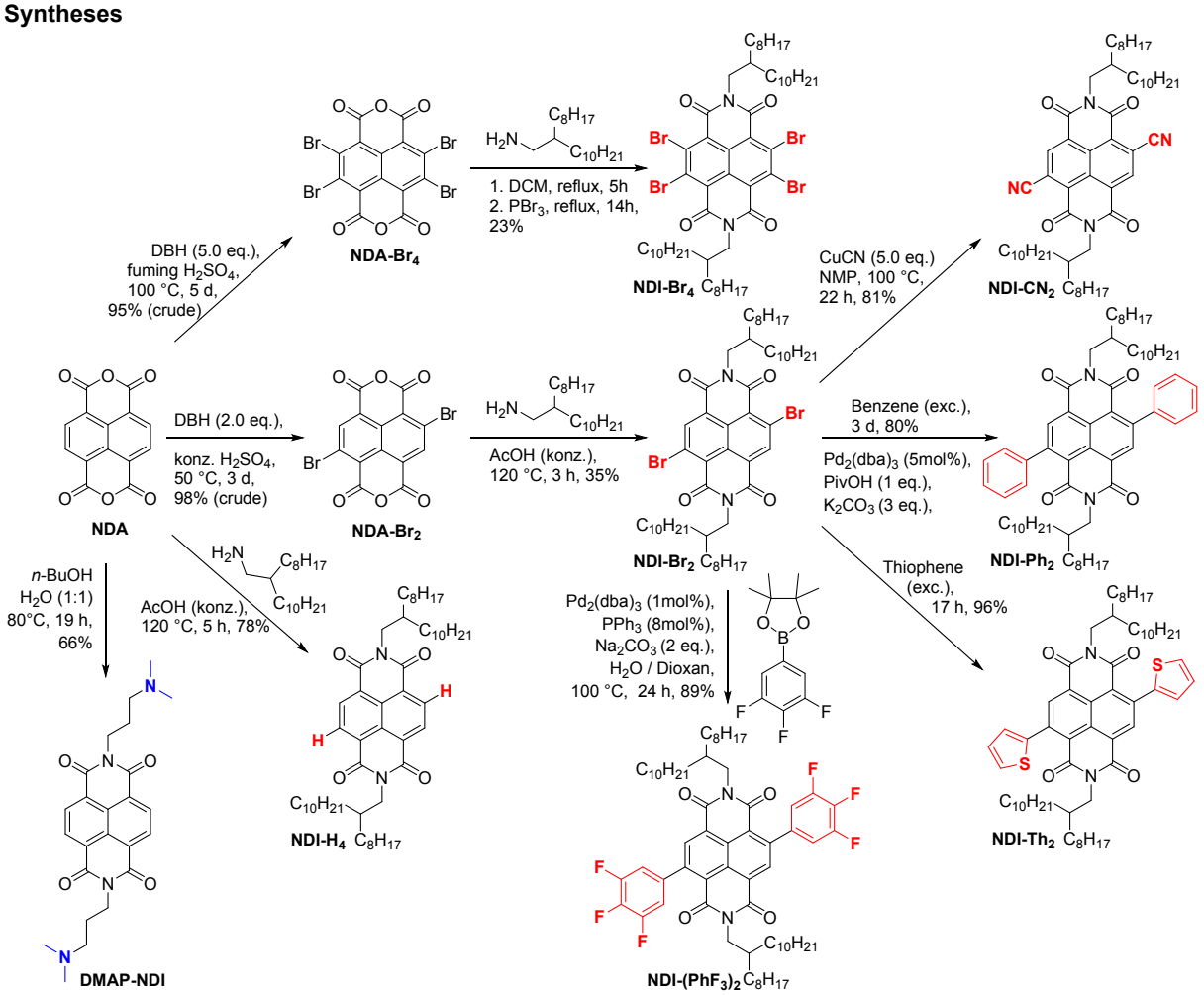
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information for

Controlling intermolecular redox-doping of naphthalene diimides

Simon B. Schmidt, Till Biskup, Xuechen Jiao, Christopher R. McNeill and Michael Sommer*

Syntheses



***Scheme S1**. Summary of the complete synthesis route to the differently core substituted NDIs.*

N,N'-bis[3-(dimethylamino)propyl]-naphthalene-1,4,5,8-bis(dicarboximide) (**DMAP-NDI**):
A mixture of naphthalenetetracarboxylic dianhydride (536 mg, 2.0 mmol) and 3-(Dimethylamino)-1-propylamine (1.23 g, 12 mmol) in water (25 mL) and *n*-Butanol (25 mL) was stirred at 80 °C overnight. After removal of the solvent under reduced pressure, the residue was dissolved in $CHCl_3$ and precipitated in MeOH, followed by recrystallization from Acetonitrile:$CHCl_3$ (10:1) to give DMAP-NDI as yellow crystal (577 mg, 66%).
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 1.92 (tt, J = 7.2 Hz, 4H, CH_2), 2.23 (s, 12H, CH_3), 2.43 (t, J = 7.2 Hz, 4H, CH_2), 4.26 (t, J = 7.5 Hz, 4H, CH_2), 8.74 (s, 4H, Ar-H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 26.11 (2C), 39.49 (2C), 45.51 (4C), 57.34 (2C), 126.78 (4C), 126.83 (2C), 131.03 (4C), 162.98 (4C) ppm.
MS (ESI, positive): m/z calc for $[MH]^+$ $C_{24}H_{29}N_4O_4$: 437.2189, found: 437.2183.

N,N'-bis(2-octyldodecyl)-2,6-di-2-thienylnaphthalene-1,4,5,8-bis(dicarboximide) (**NDI-Th$_2$**):
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 0.8-4.2 (82H, Alkyl-H), 7.19 (dd, J = 5.1, 3.6 Hz, 2H, Th-H), 7.30 (dd, J = 3.6, 1.2 Hz, 2H, Th-H), 7.56 (dd, J = 5.1, 1.2 Hz, 2H, Th-H), 8.76 (s, 2H, Ar-H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 14.24 (4C), 22.80 (4C), 26.51 (4C), 29.4-30.2 (16C), 31.70 (4C), 32.03 (4C), 36.58 (2C), 45.01 (2C), 123.50 (2C), 125.53 (2C), 127.54 (2C), 127.59 (2C), 128.16 (2C), 128.37 (2C), 136.76 (2C), 140.35 (2C), 140.94 (2C), 162.48 (2C), 162.67 (2C) ppm.
MS (ESI, positive): m/z calc for $[MH]^+$ $C_{62}H_{91}N_2O_4S_2$: 991.6420, found: 991.6428.

N,N'-bis(2-octyldodecyl)-2,6-diphenylnaphthalene-1,4,5,8-bis(dicarboximide) (**NDI-Ph$_2$**):
Synthesis of NDI-Ph_2 was done as a direct C-H arylation reaction.
To NDI-Br_2 (98.1 mg, 0.10 mmol), K_2CO_3 (41.5 mg), 0.30 mmol, 3 eq.), Pivalic acid (10.21 mg, 0.10 mmol, 1 eq.) and Pd_2dba_3 (4.58 mg, 5.0 µmol, 5 mol%) under argon degassed benzene (1 mL) was added, this mixture was stirred for 3 days in a closed vial at 105 °C. The excess benzene was removed under reduced pressure and the residue was filtered with $CHCl_3$ over neutral aluminium oxide to give NDI-Ph_2 as yellow solid. (78 mg, 80%).
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 0.8-4.1 (82H, Alkyl-H), 7.39-7.54 (m, 10H, Ph-H_5), 8.66 (s, 2H, Ar-H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 14.35 (4C), 22.90 (2C), 22.92 (2C), 26.57 (4C), 29.5-30.3 (16C), 31.73 (2C), 31.75 (2C), 32.12 (2C), 32.14 (2C), 36.63 (2C), 44.93 (2C), 123.20 (2C), 125.81 (2C), 127.46 (2C), 128.32 (4C), 128.52 (2C), 128.64 (4C), 136.06 (2C), 140.78 (2C), 147.91 (2C), 162.88 (2C), 163.13 (2C) ppm.
MS (ESI, positive): m/z calc for $[MH]^+$ $C_{66}H_{95}N_2O_4$: 979.7292, found: 979.7281.

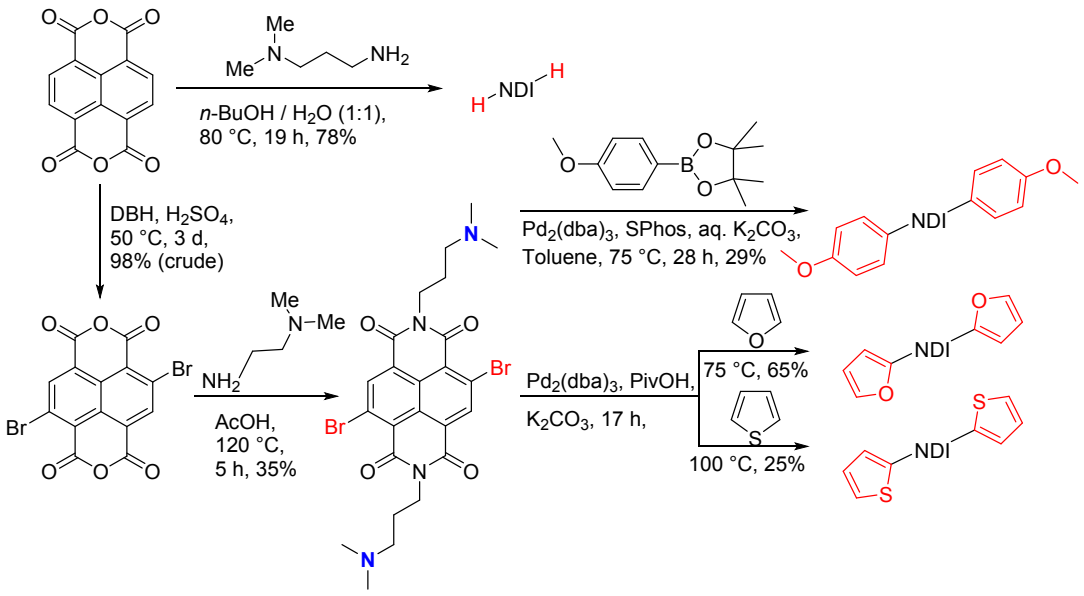
N,*N*′-bis(2-octyldodecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (**NDI-Br$_2$**):
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 0.8-4.2 (82H, Alkyl-H), 8.99 (s, 2H, Ar-H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 14.26 (4C), 22.81 (2C), 22.84 (2C), 26.48 (4C), 29.4-30.2 (16C), 31.70 (4C), 32.03 (2C), 32.07 (2C), 36.61 (2C), 45.60 (2C), 124.24 (2C), 125.44 (2C), 127.90 (2C), 128.52 (2C), 139.31 (2C), 161.18 (2C), 161.33 (2C) ppm.

N,*N*′-bis(2-octyldodecyl)-2,3,6,7-tetrabromonaphthalene-1,4,5,8-bis(dicarboximide) (**NDI-Br$_4$**):
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 0.8-4.2 (82H, Alkyl-H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 14.25 (4C), 22.80 (2C), 22.82 (2C), 26.43 (4C), 29.4-32.1 (16C), 31.70 (4C), 32.03 (2C), 32.05 (2C), 36.67 (4C), 46.77 (2C), 125.92 (4C), 126.48 (2C), 135.39 (4C), 160.34 (4C) ppm.
MS (ESI, negative): m/z calc for $[M]^-$ $C_{54}H_{82}N_2O_4Br_4$: 1142.2967, found: 1142.2973.

N,*N*′-bis(2-octyldodecyl)-2,6-bis(3,4,5-trifluorophenyl)-naphthalene-1,4,5,8-bis(dicarboximide) (**NDI-(PhF$_3$)$_2$**):
Syntheses of NDI-$(PhF_3)_2$ was done as a Suzuki coupling reaction: To Br_2NDI (98.1 mg, 0.10 mmol), Na_2CO_3 (21.2 mg, 0.20 mmol, 2 eq.), Pd_2dba_3 (0.92 mg, 1.0 µmol, 1 mol%) and PPh_3 (2.10 mg, 8.0 µmol, 8mol%) under argon degassed 1,4-dioxan (0.33 mL) and *m,m,p-Trifluorbenzol*-BPin (114 mg, 0.40 mmol, 4 eq.) were added, stirred for 10 min, then degassed H_2O (0.11 mL) was added and the reaction mixture was stirred for 24 hours at 100 °C. After cooling to room temperature the solution was crushed out into Methanol (5 mL) and the precipitate purified over a short silica filter from $CHCl_3$ to give NDI-$(PhF_3)_2$ as pale yellow solid. (96 mg, 88%).
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 0.8-4.1 (82H, Alkyl-H), 6.95-7.04 (m, 4H, Ph-H_2), 8.59 (s, 2H, Ar-H) ppm.
^{19}F NMR (600 MHz, $CDCl_3$, 25°C): δ = -160.11 (2F), -133.48 (4F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 14.23 (4C), 22.79 (2C), 22.81 (2C), 26.43 (4C), 29.4-30.2 (16C), 31.66 (2C), 31.67 (2C), 32.02 (2C), 32.04 (2C), 36.61 (2C), 45.12 (2C), 112.71 (4C), 112.84 (4C), 123.44 (2C), 126.10 (2C), 127.51 (2C),135.27 (2C), 144.73 (2C), 150.54 (2C), 152.20 (2C), 162.24 (2C), 162.35 (2C) ppm.
MS (ESI, negative): m/z calc for $[M]^-$ $C_{66}H_{88}F_6N_2O_4$: 1086.6648, found: 1086.6655,
m/z calc. for $[MCl]^-$ $C_{66}H_{88}F_6N_2O_4Cl$: 1121.6337, found: 1121.6340.

N,*N*′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide) (**NDI-H$_4$**):
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 0.8-4.2 (82H, Alkyl-H), 8.75 (s, 4H, Ar-H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 14.25 (4C), 22.79 (2C), 22.82 (2C), 26.57 (4C), 29.4-30.2 (16C), 31.79 (4C), 32.02 (2C), 32.05 (2C), 36.76 (2C), 45.11 (2C), 126.72 (4C), 126.88 (2C), 131.15 (4C), 160.35 (4C) ppm.
MS (ESI, negative): m/z calc for $[M]^-$ $C_{54}H_{86}N_2O_4$: 826.6588, found: 826.6597.

N,*N*′-bis(2-octyldodecyl)-2,6-dicyanonaphthalene-1,4,5,8-bis(dicarboximide) (**NDI-CN$_2$**):
Synthesis of NDI-CN_2 was done as a Rosenmund–von Braun reaction.
Crude NDI-Br_2 (without purification after the imidisation reaction of NDA-Br_2, contains ca. 20mol% BrNDI and Br_3NDI, which can be separated as NDI-CN and NDI-CN_3) (986 mg, 1.0 mmol) and CuCN (450 mg, 5.0 mmol, 5.0 eq.) were stirred for 24 h in NMP (60 mL) at 110 °C. The reaction mixture was precipitated in water (300 mL), the solid was collected through filtration and purified by column chromatographie (SiO_2, iHex:EE, 5:1) to give NDI-CN_2 as yellow powder (555 mg, 79%).
^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 0.8-4.2 (82H, Alkyl-H), 9.04 (s, 2H, Ar-H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 14.24 (4C), 22.79 (2C), 22.80 (2C), 26.40 (4C), 29.4-30.2 (16C), 31.59 (4C), 31.99 (2C), 32.03 (2C), 36.61 (2C), 45.93 (2C), 115.92 (2C), 116.97 (2C), 127.25 (2C), 127.64 (2C), 128.68 (2C), 136.18 (2C), 160.15 (2C), 160.56 (2C) ppm.
MS (APCI, positive): m/z calc for $[MNH_4]^+$ $C_{56}H_{88}N_5O_4$: : 894.6836, found: 894.6838.



Scheme S2. *Series of NDI derivatives with dimethylaminopropyl (DMAP) side chains and core substituents of different electron withdrawing strength.*

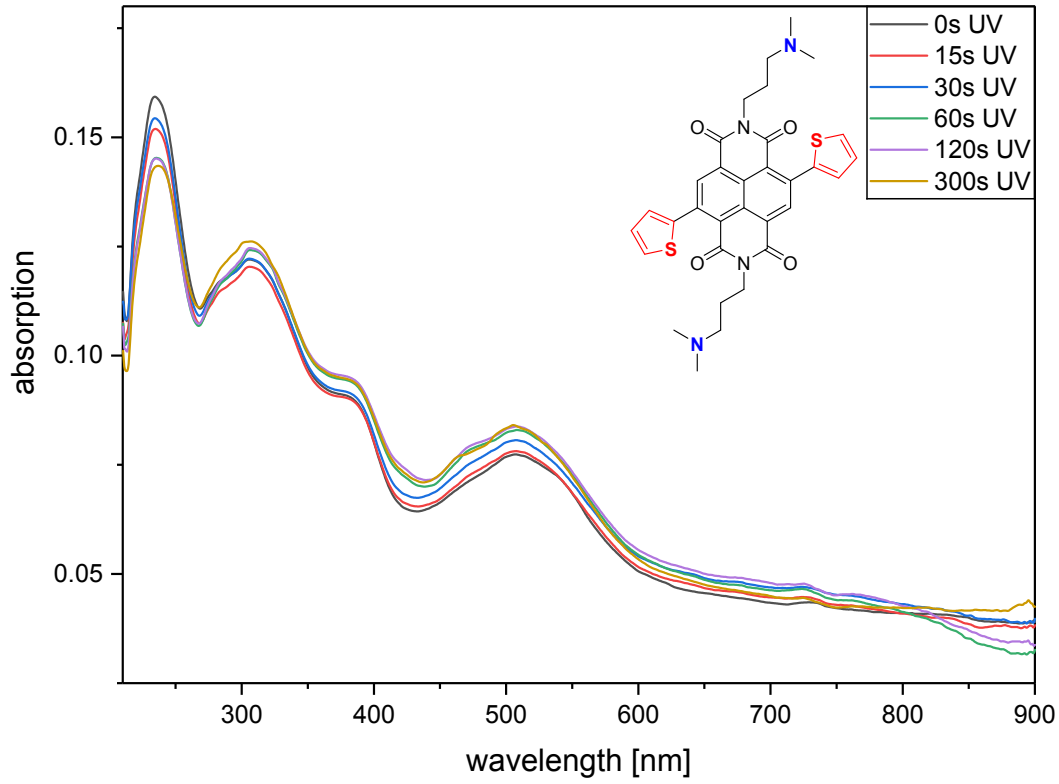


Figure S1. *Thin film UV-Vis spectra of pure DMAP-NDI-Th$_2$ in argon atmosphere. The compound does not develop detectable amounts of radical anion absorption bands upon UV (366 nm) irradiation.*

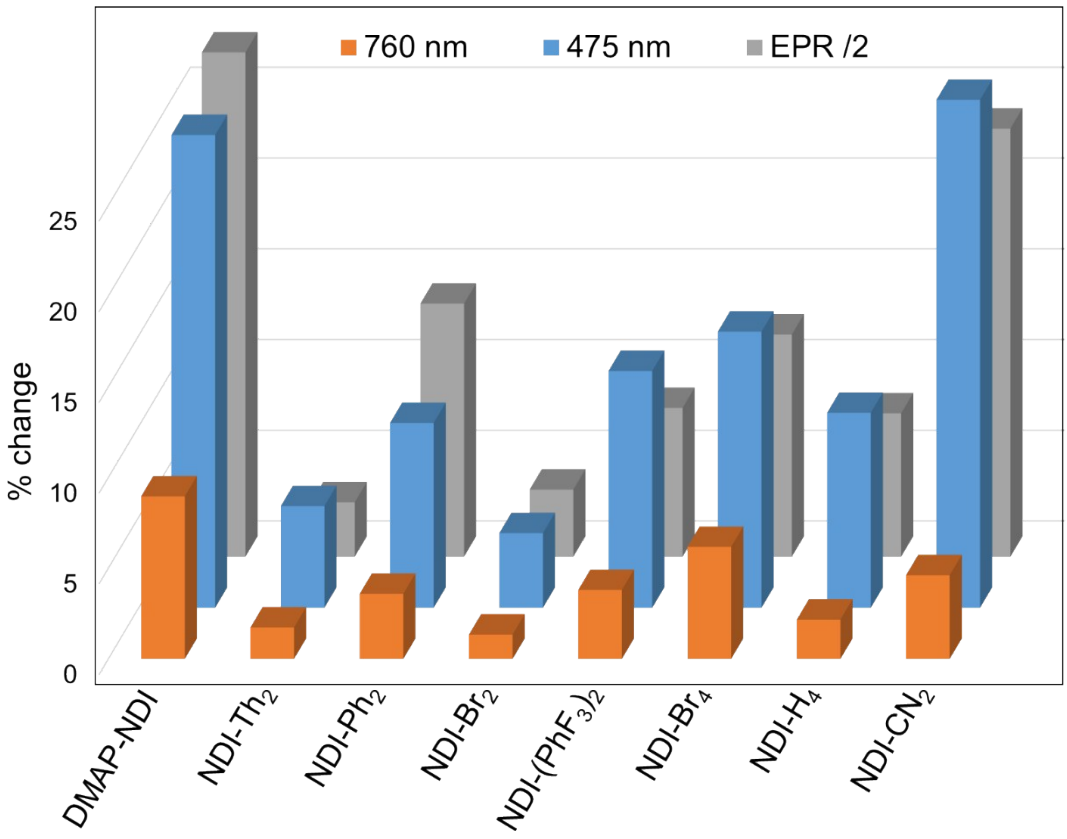


Figure S2. *Increase of the radical anions' UV-vis absorption maxima of NDI-X$_2$Y$_2$ 1:1 mixtures with DMAP-NDI after 5 min of UV irradiation in comparison with EPR signal intensity (absolute value /2[a.u.]).*

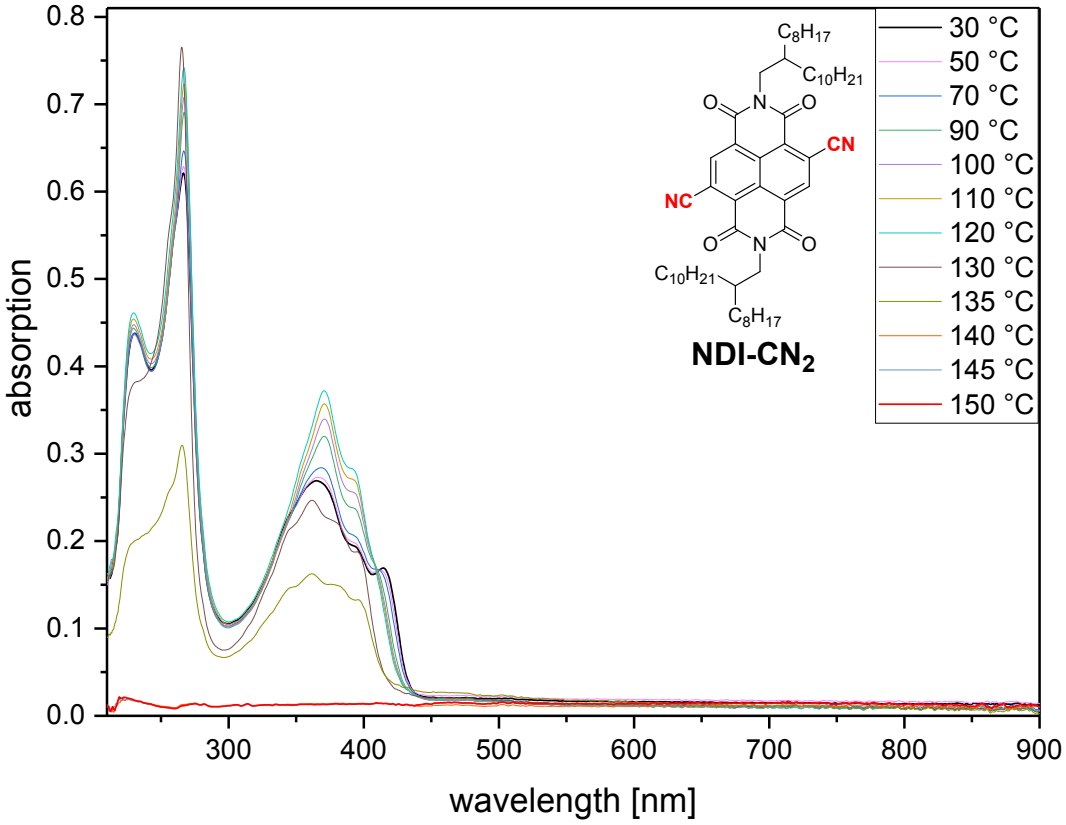


Figure S3. *Temperature dependent thin film UV-Vis spectra of pure NDI-CN_2 in argon atmosphere. The compound evaporates at elevated temperatures.*

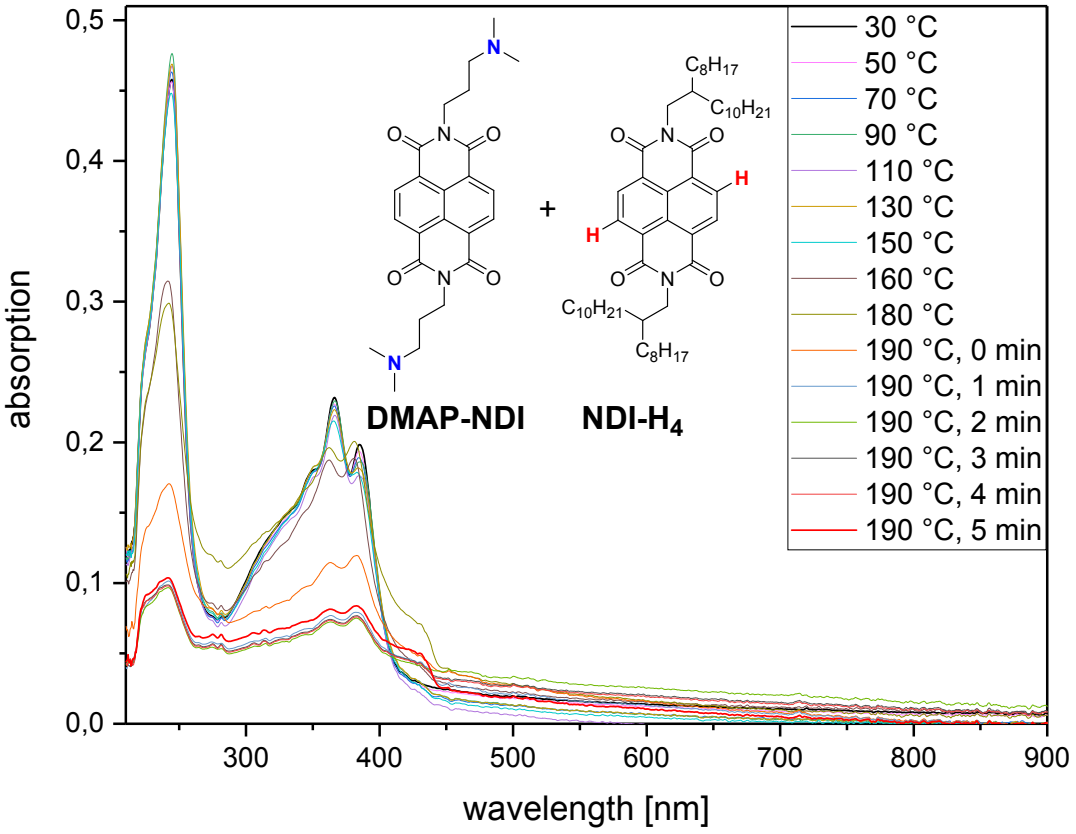


Figure S4. *Temperature dependent thin film UV-Vis spectra of a DMAP-NDI / NDI-H_4 mixture (1:1, mol:mol) in argon atmosphere. The compounds evaporate at elevated temperatures without developing radical anion absorption bands.*

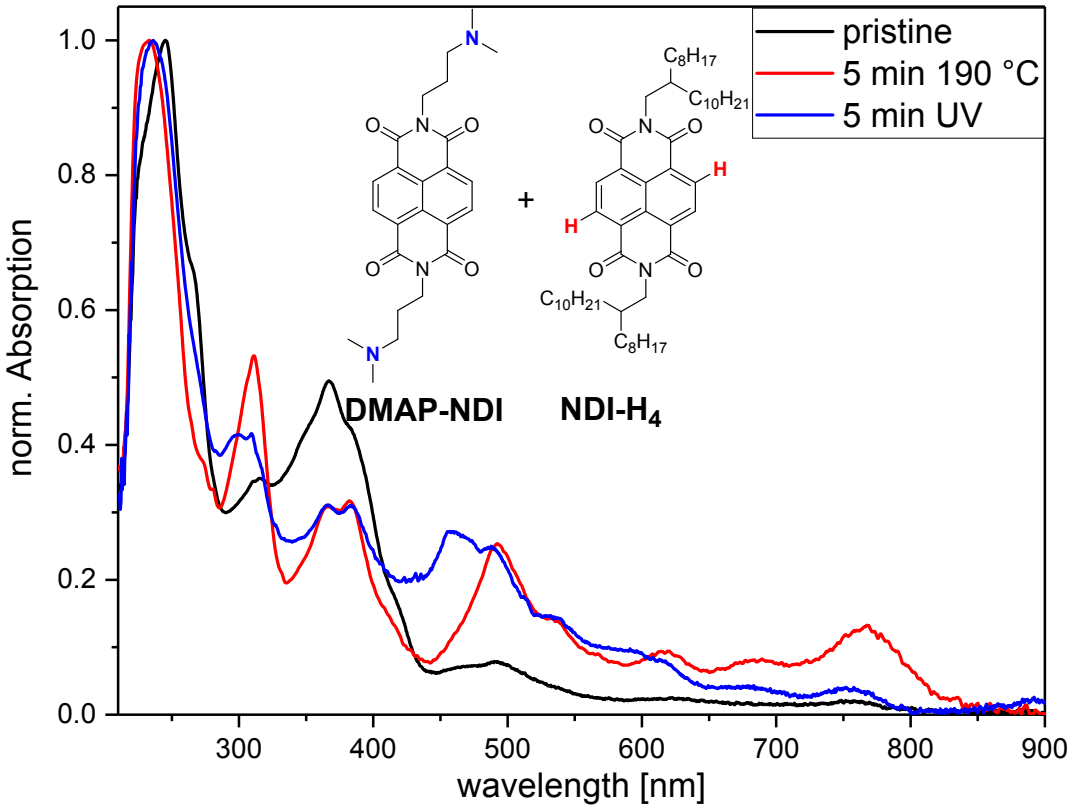


Figure S5. *Thin film UV-Vis absorption comparison of UV light (366 nm) and thermally activated DMAP-NDI / NDI-H_4 mixtures (1:1, mol:mol) in argon atmosphere.*

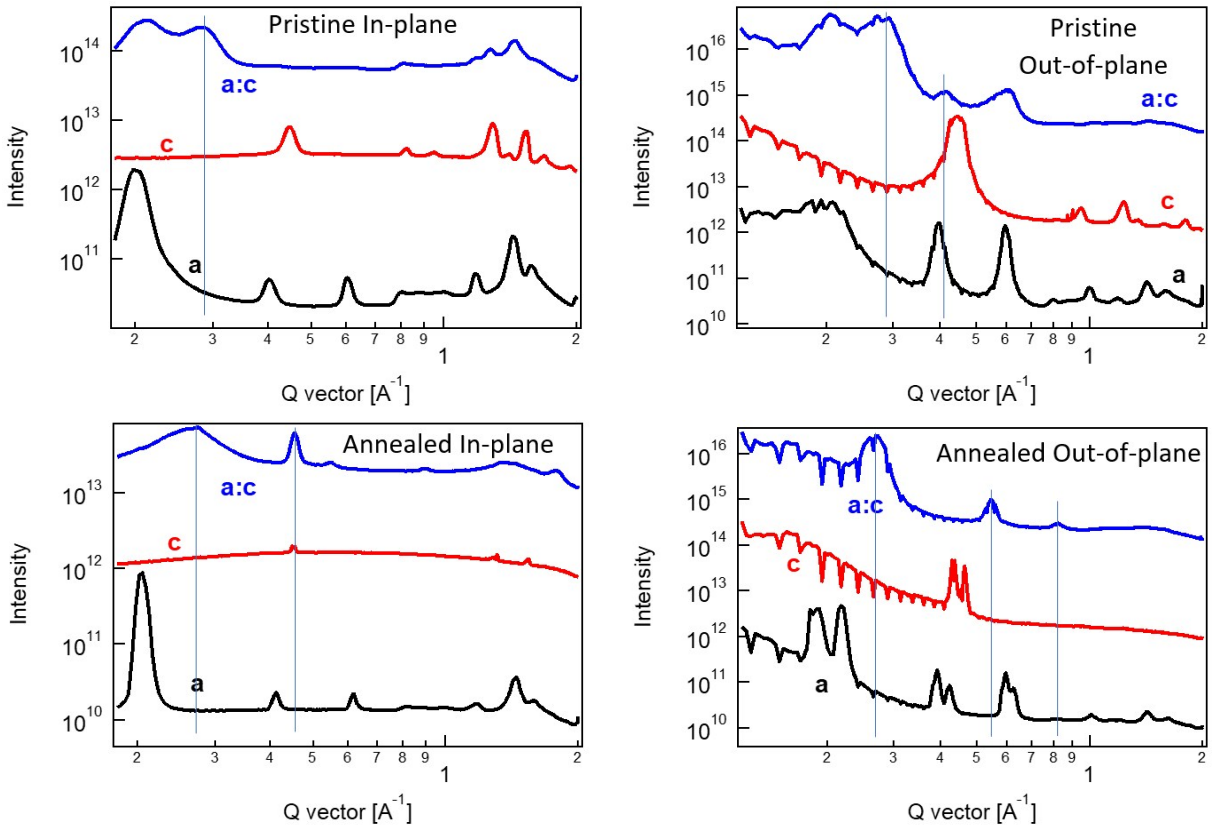


Figure S6*. 1-dimensional traces extracted from GIWAXS measurements of pure DMAP-NDI (a), NDI-CN_2 (c) and the 1:1 mix of both (a:c) along the in-plane (left) and out-of-plane (right) directions for pristine samples (top) and annealed (bottom) with new peaks in the blend highlighted by thin blue lines.*

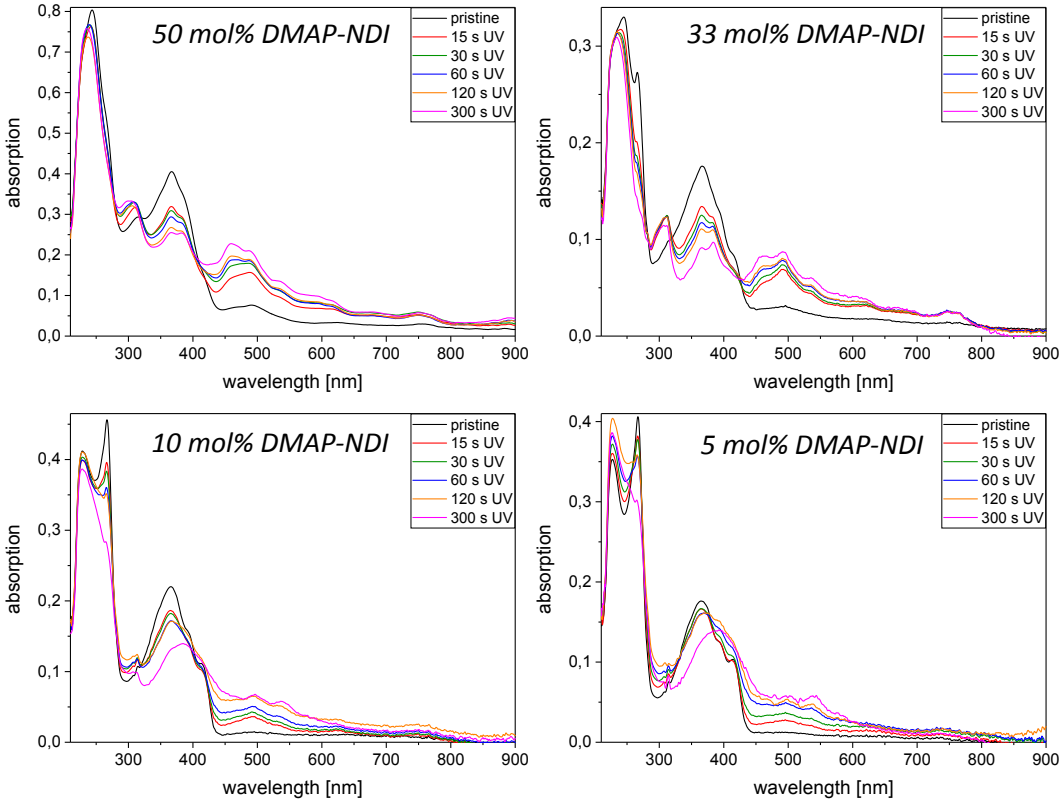


Figure S7. *Thin film UV-Vis absorption comparison of NDI-CN_2 mixed with different ratios DMAP-NDI in argon atmosphere.*

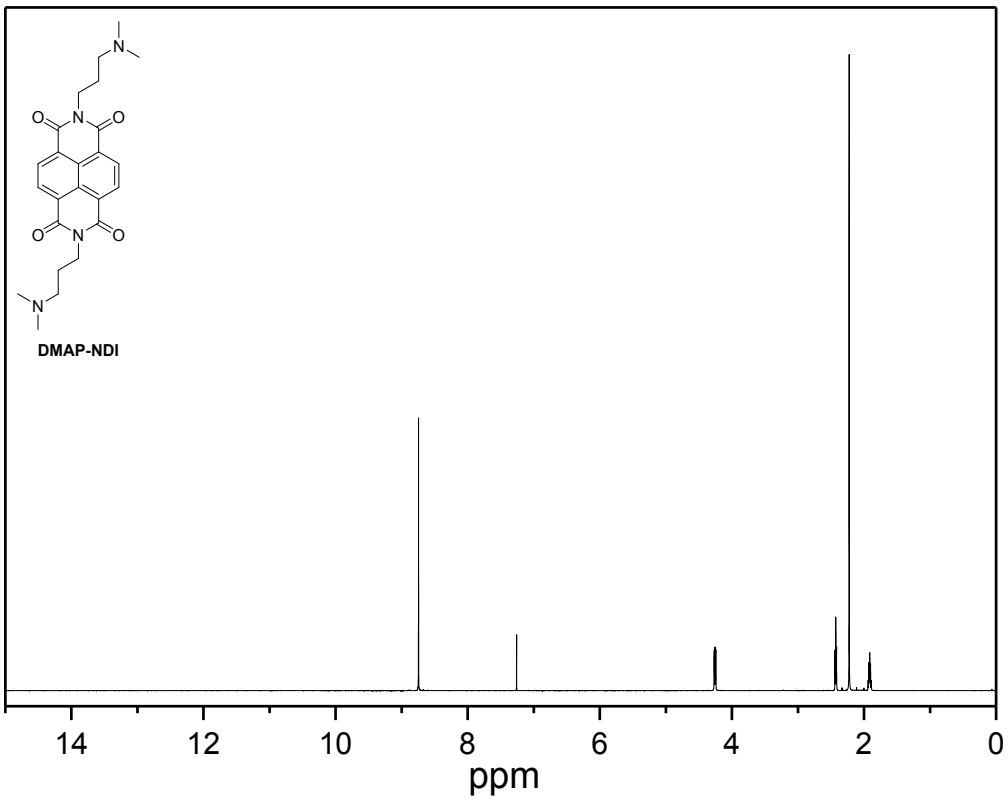


Figure S8. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of DMAP-NDI.*

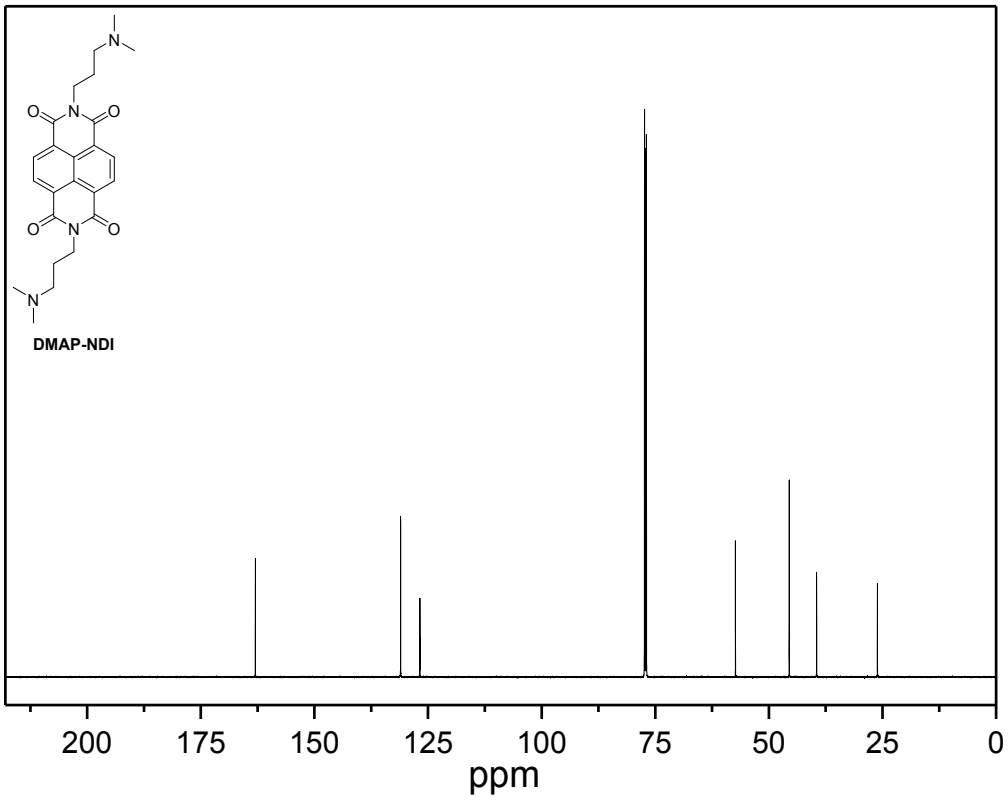


Figure S9. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of DMAP-NDI.*

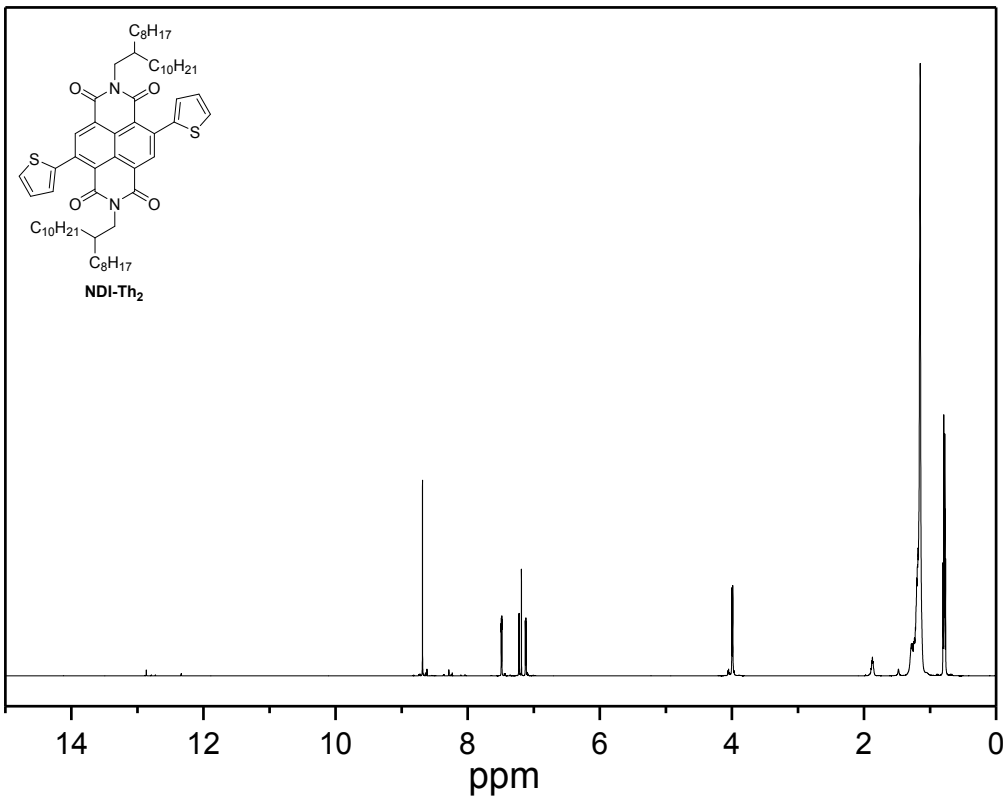


Figure S10. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of NDI-Th_2.*

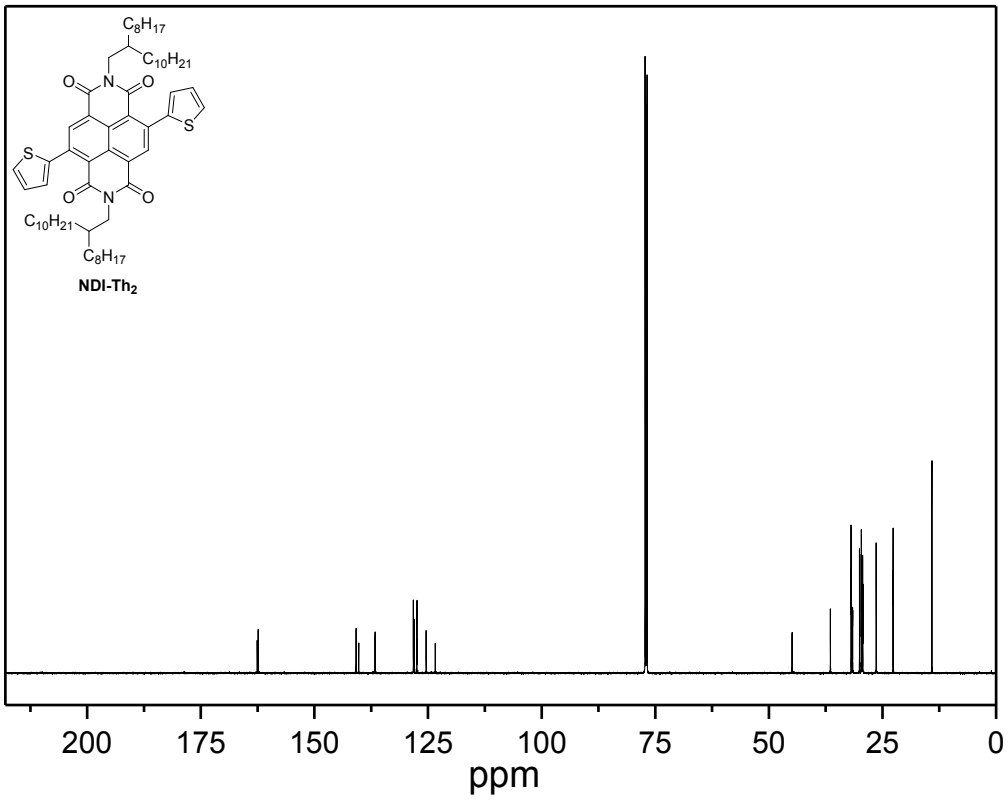


Figure S11. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of NDI-Th_2.*

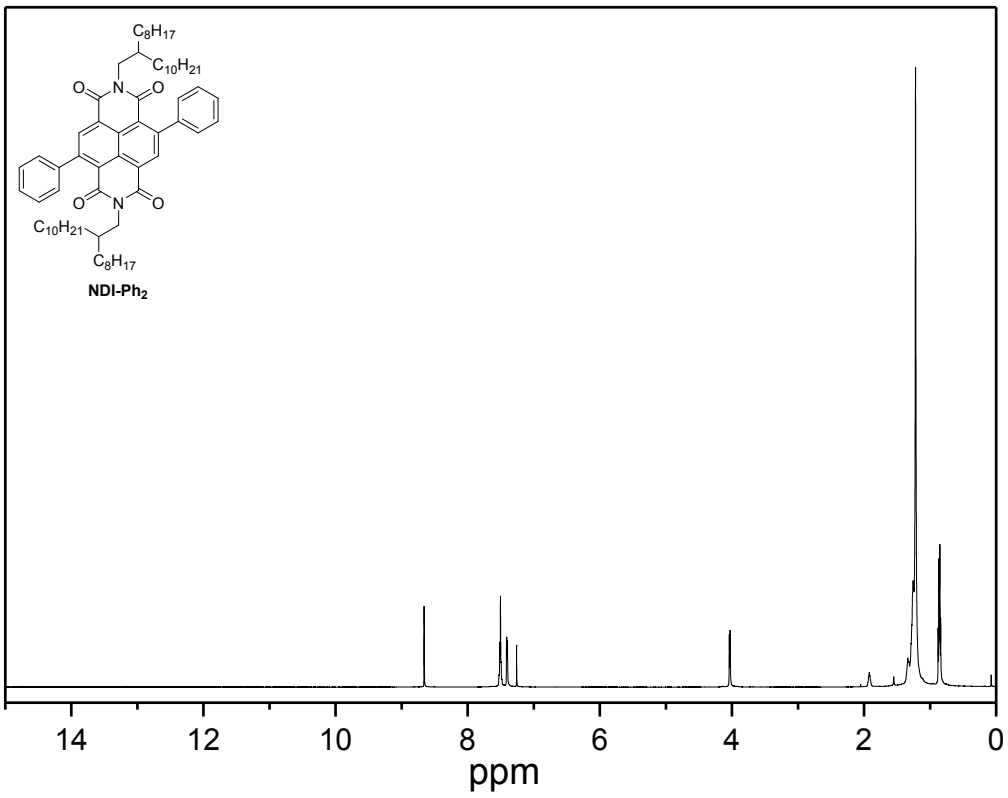


Figure S12. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of NDI-Ph_2.*

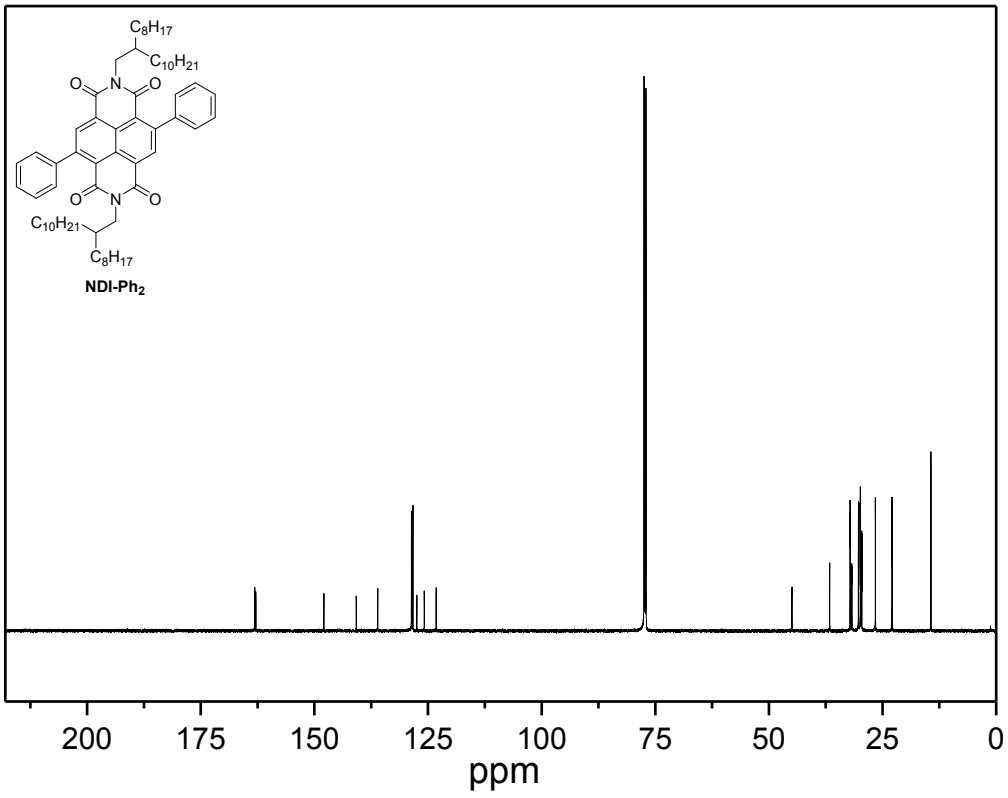


Figure S13. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of NDI-Ph_2.*

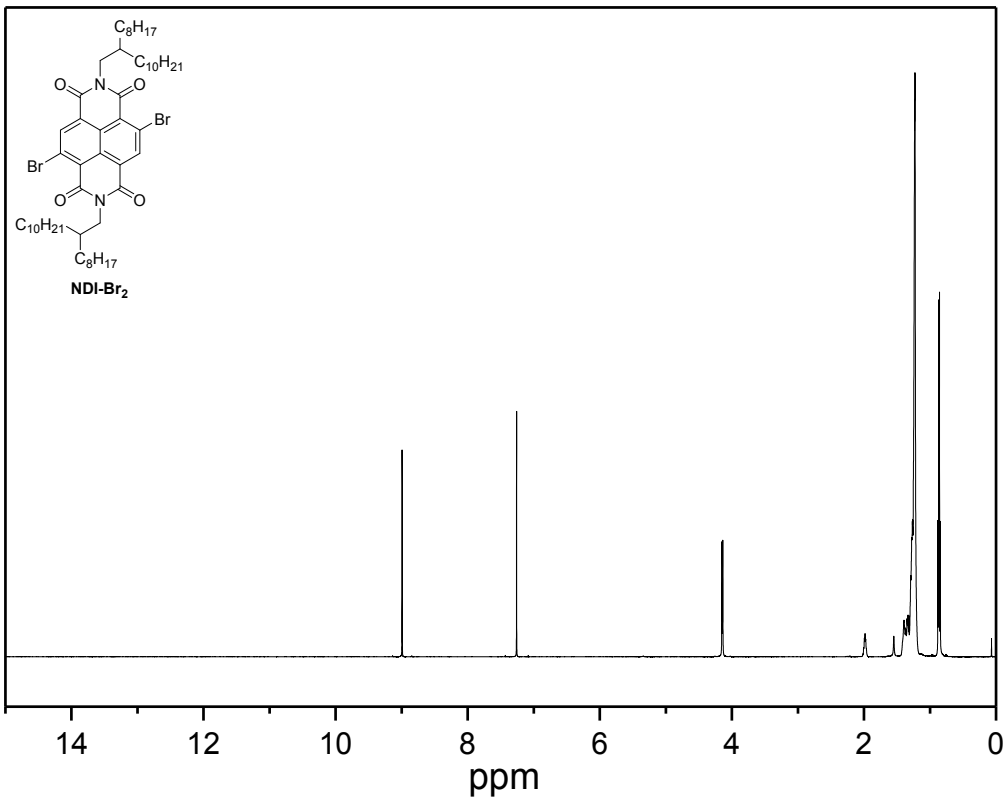


Figure S14. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of NDI-Br_2.*

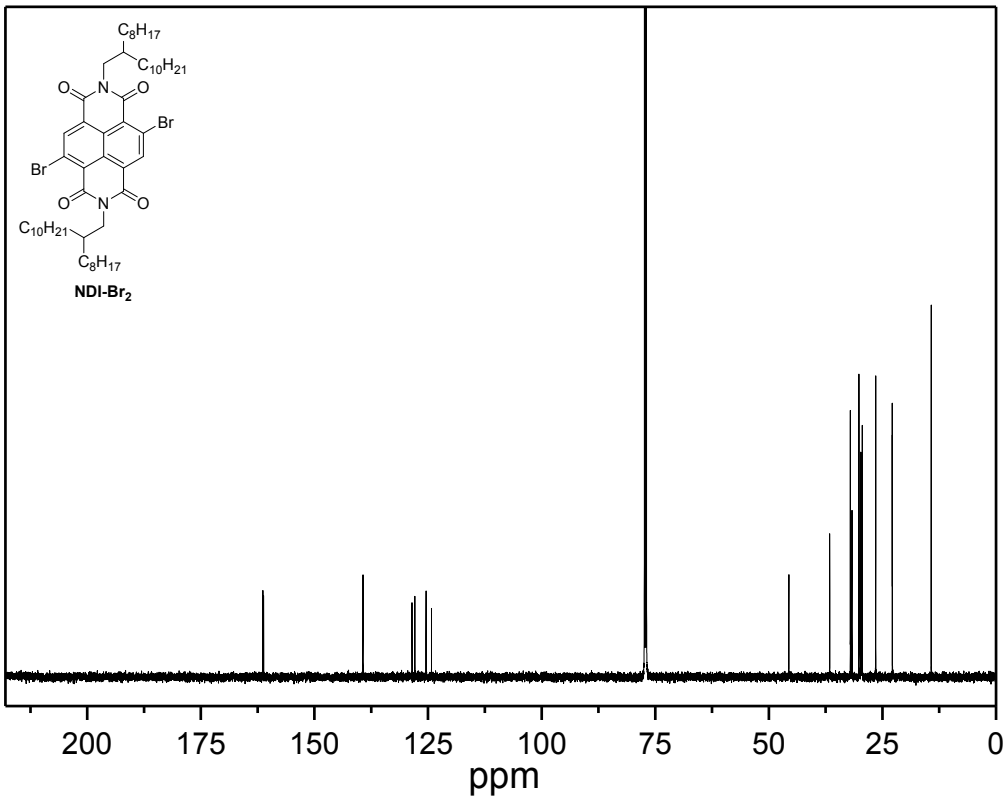


Figure S15. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of NDI-Br_2.*

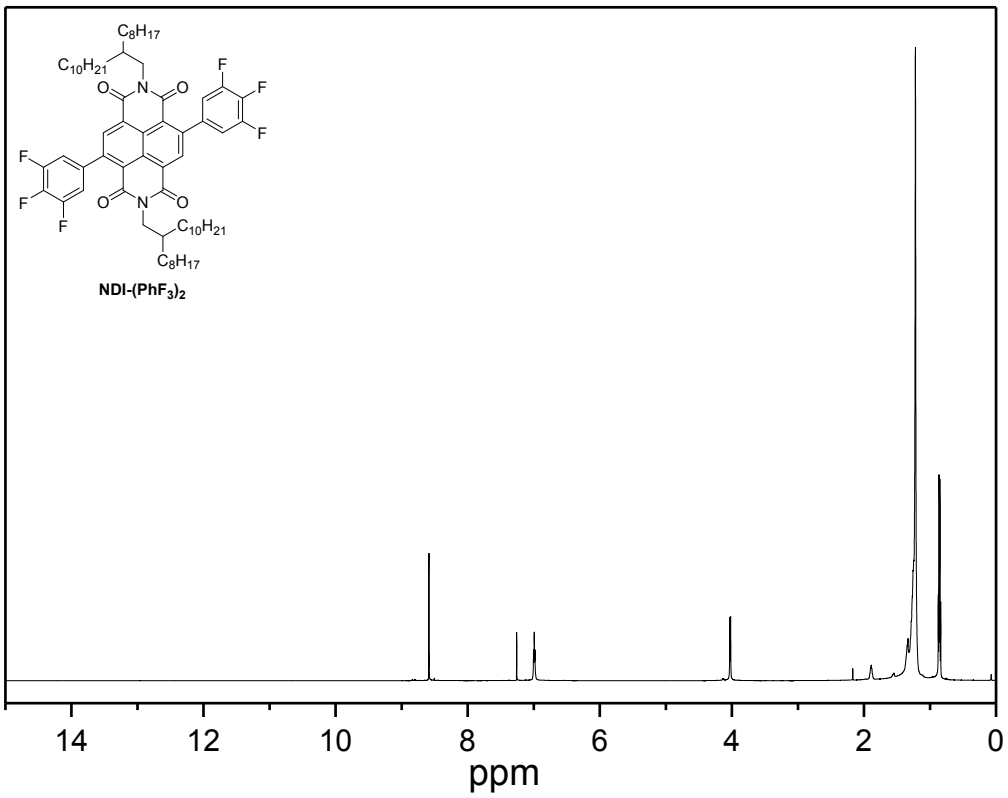


Figure S16. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of NDI-$(PhF_3)_2$.*

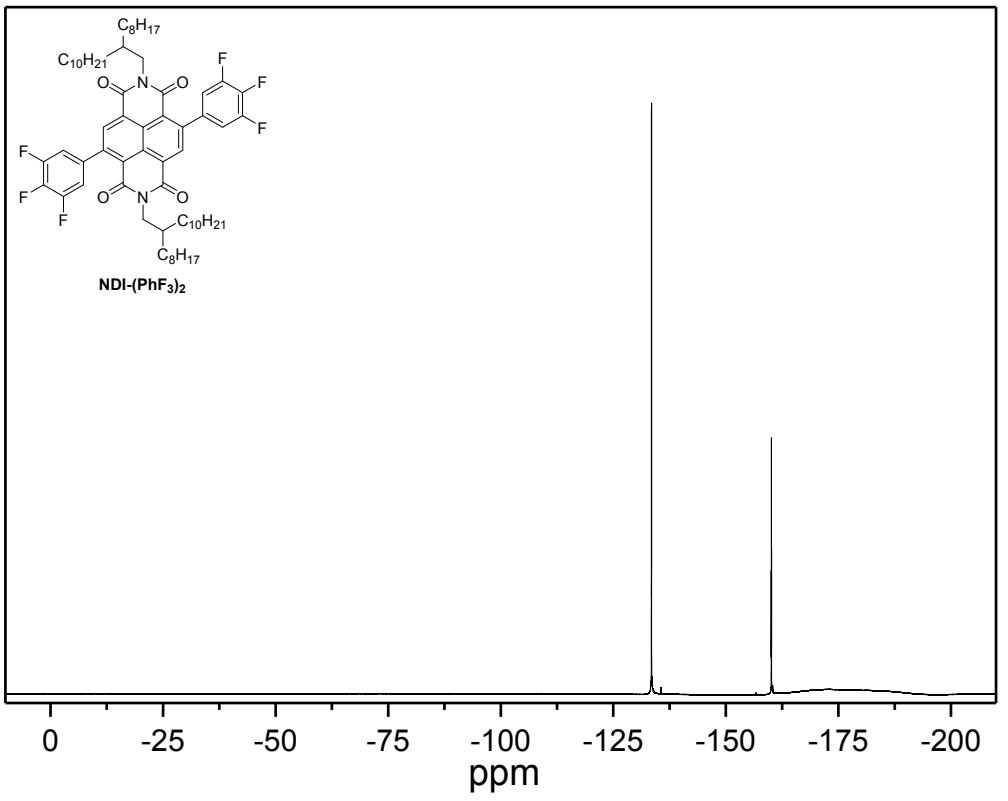


Figure S17. *^{19}F NMR (600 MHz, RT, $CDCl_3$) of NDI-$(PhF_3)_2$.*

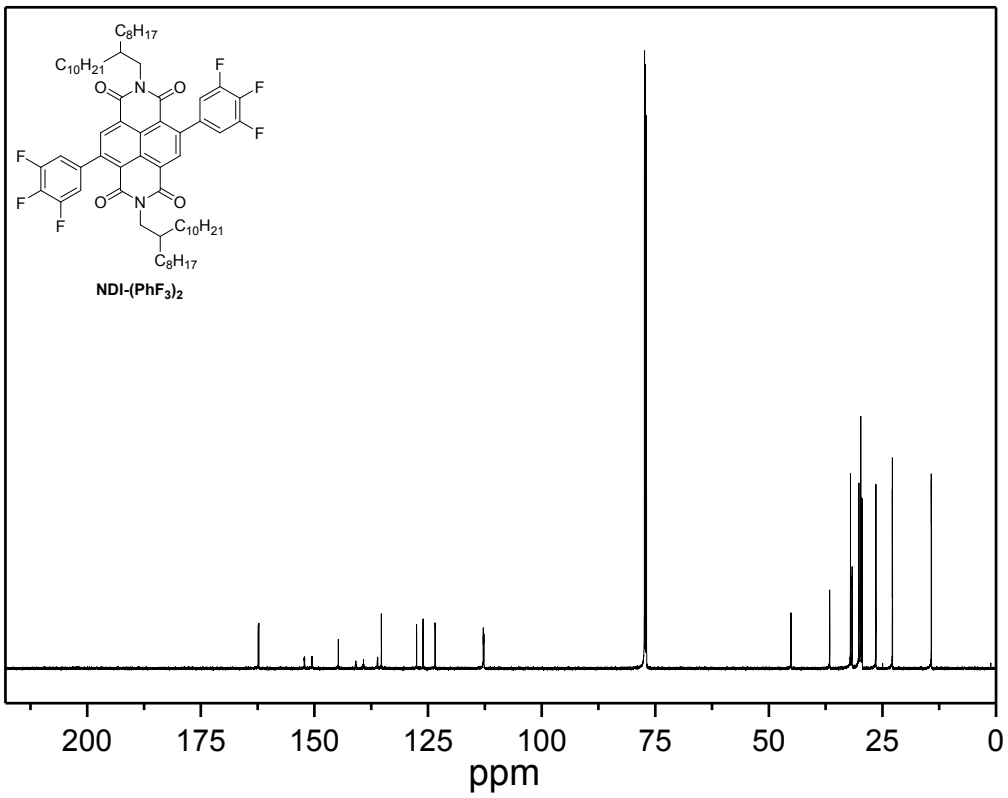


Figure S18. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of NDI-$(PhF_3)_2$.*

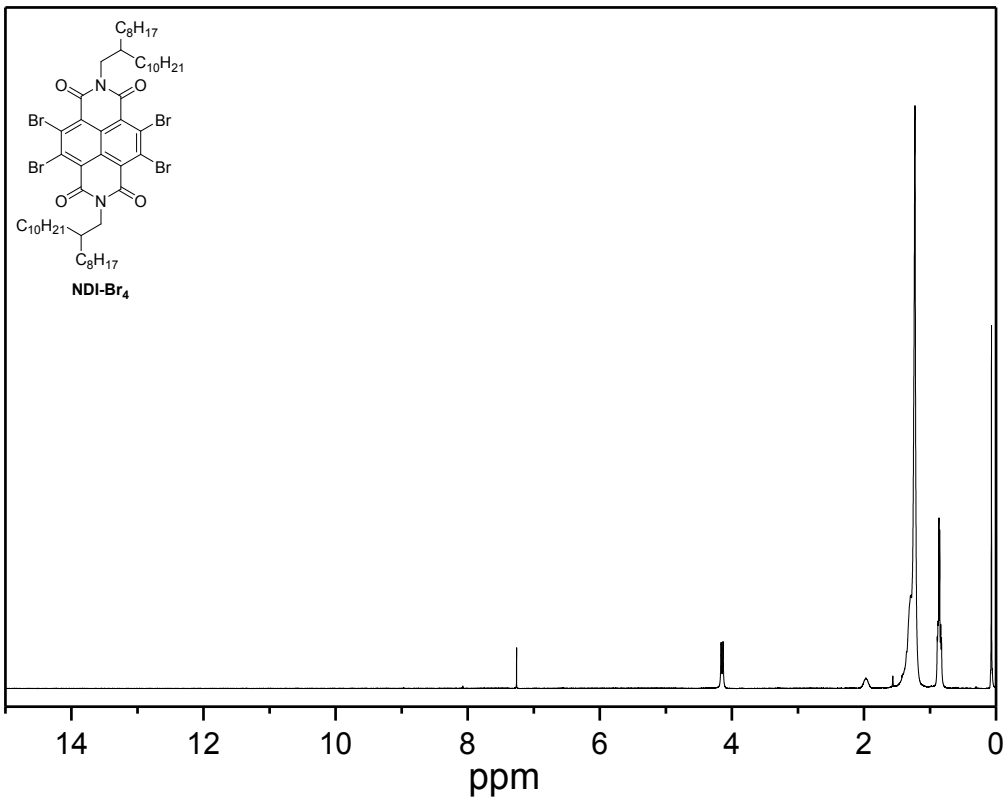


Figure S19. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of NDI-Br_4.*

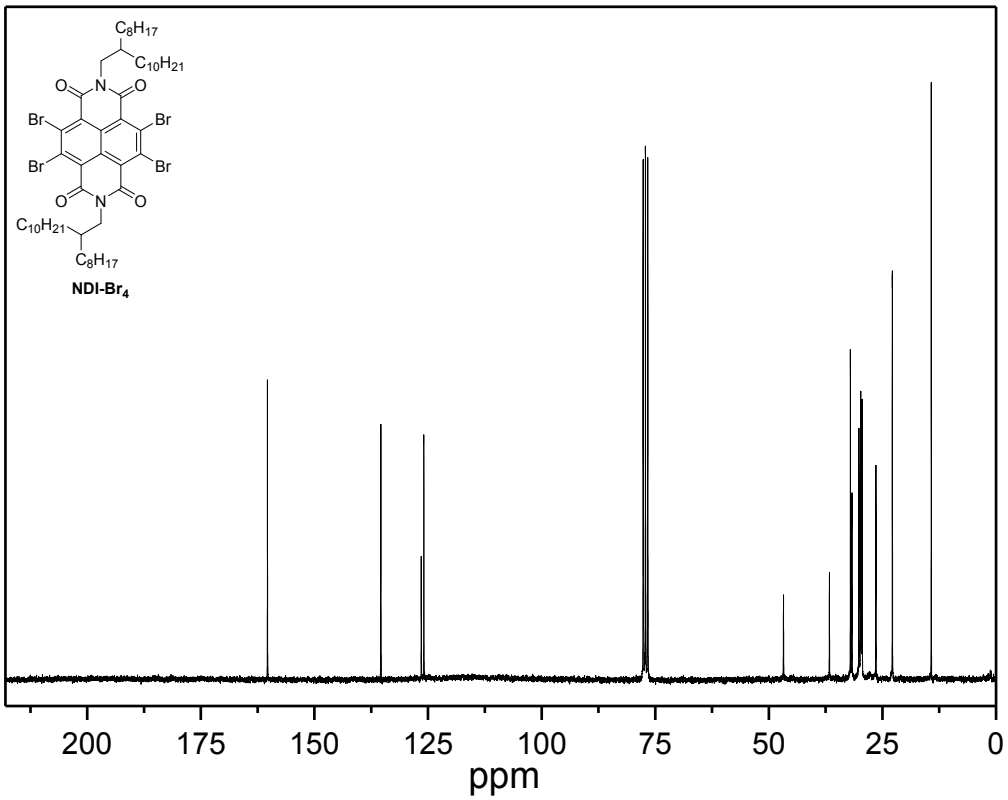


Figure S20. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of NDI-Br_4.*

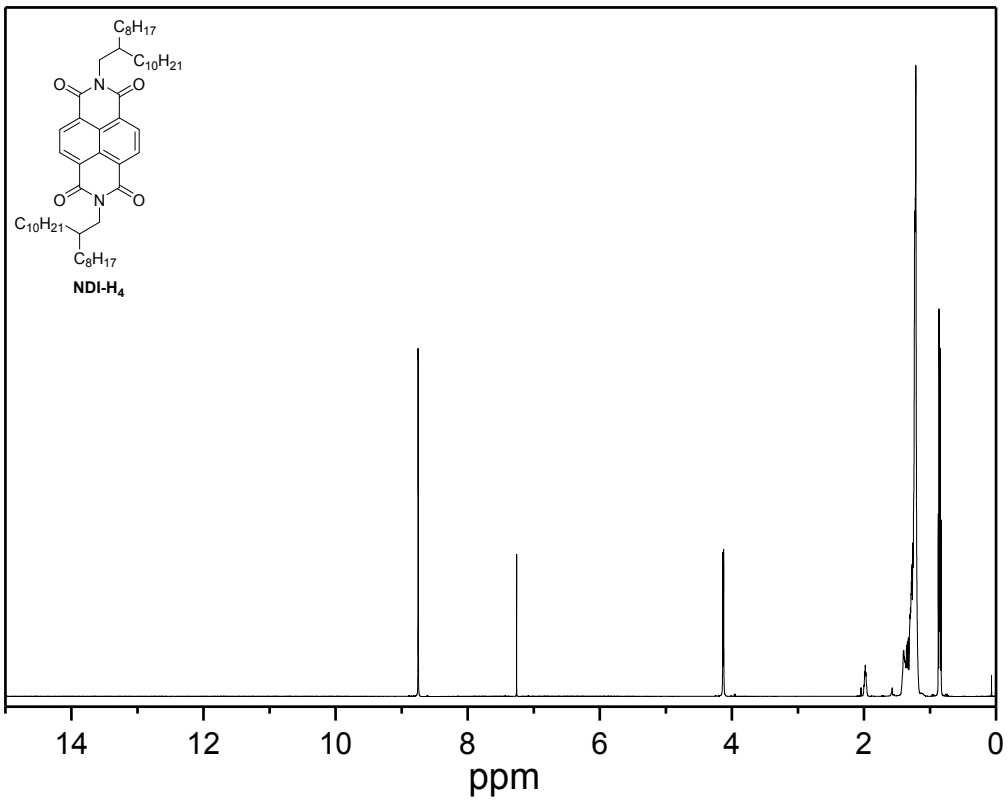


Figure S21. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of NDI-H_4.*

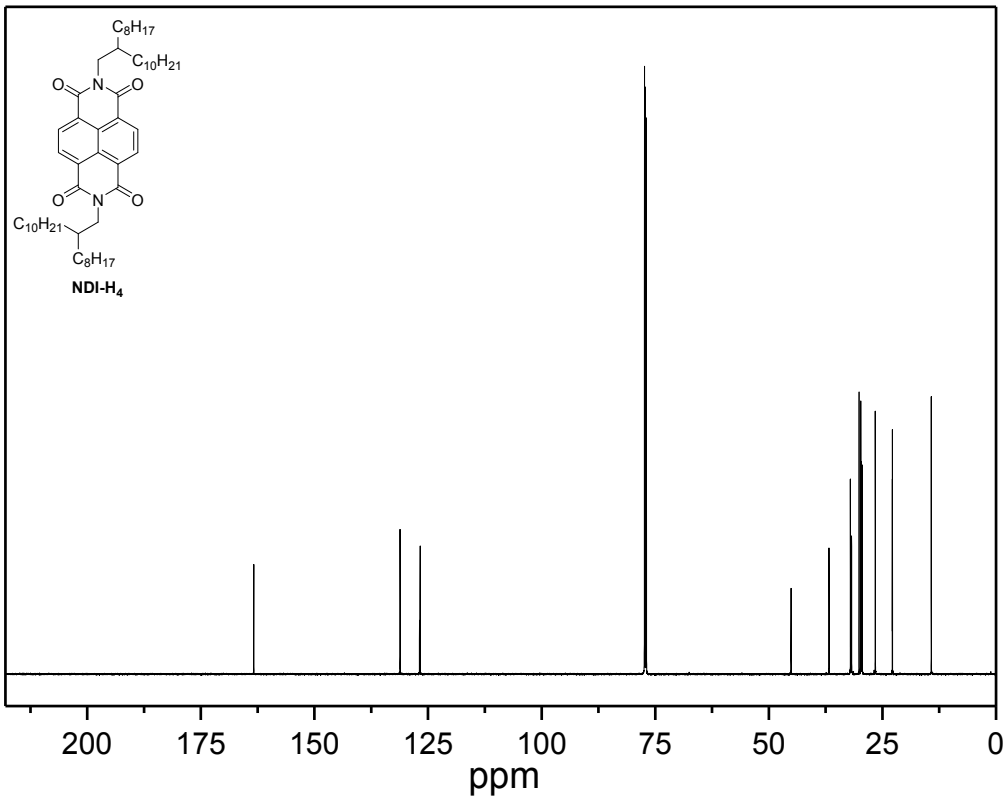


Figure S22. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of NDI-H_4.*

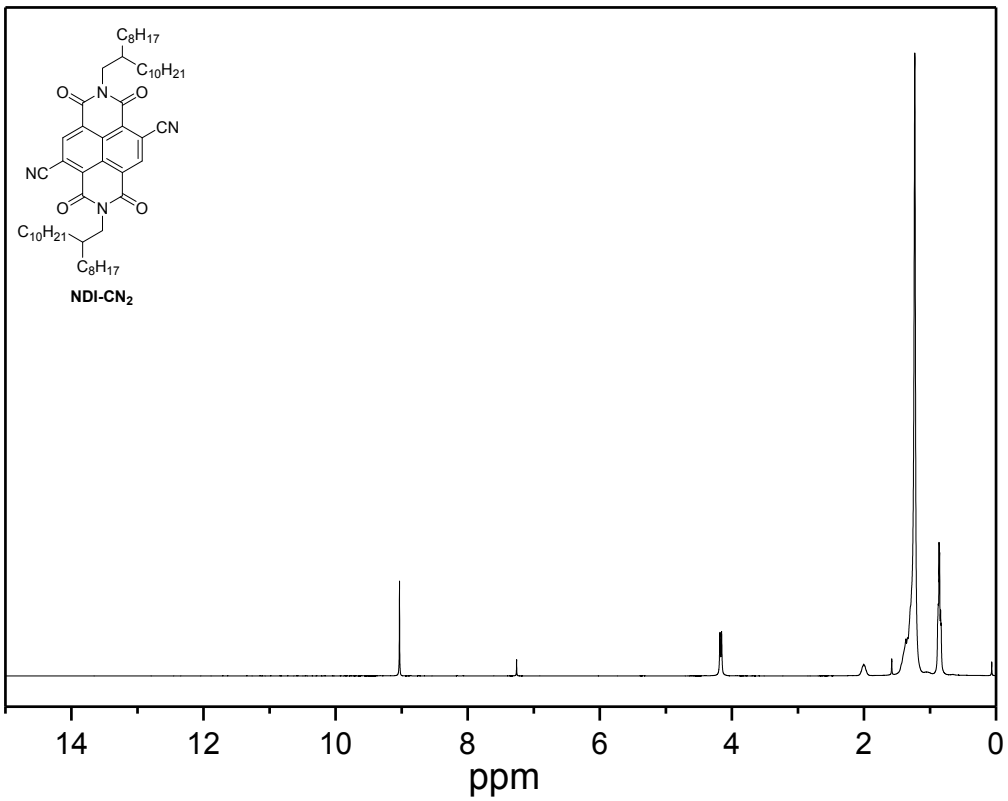


Figure S23. *^{1}H NMR (600 MHz, RT, $CDCl_3$) of NDI-CN_2.*

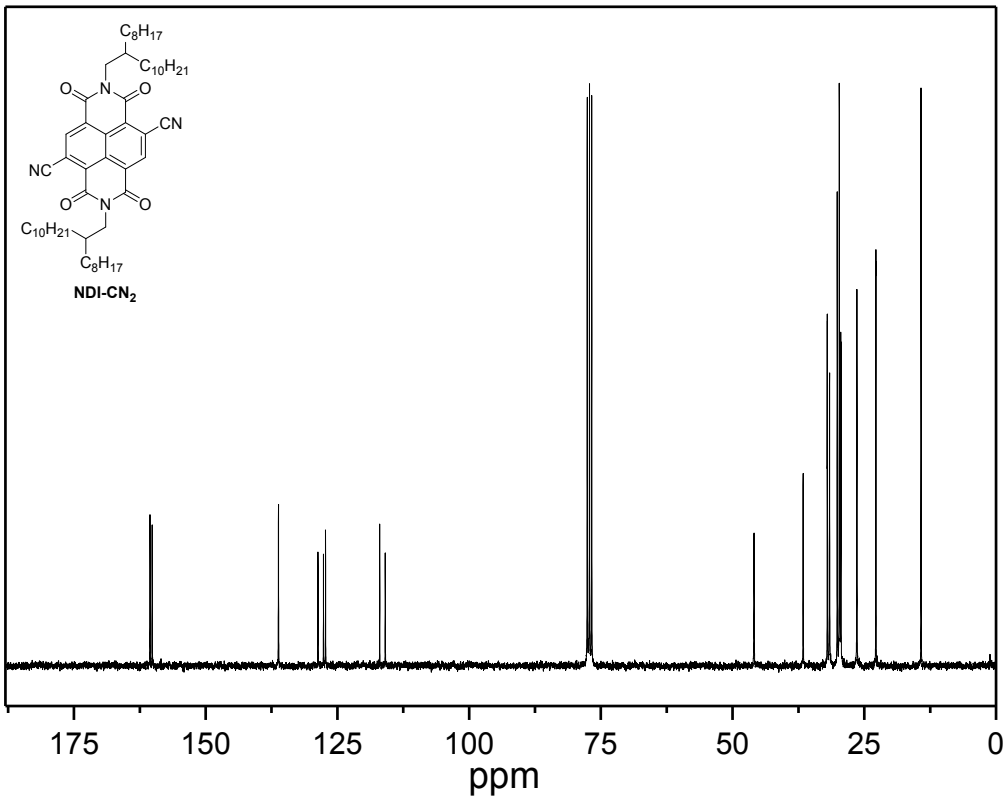


Figure S24. *^{13}C NMR (150.9 MHz, RT, $CDCl_3$) of NDI-CN_2.*

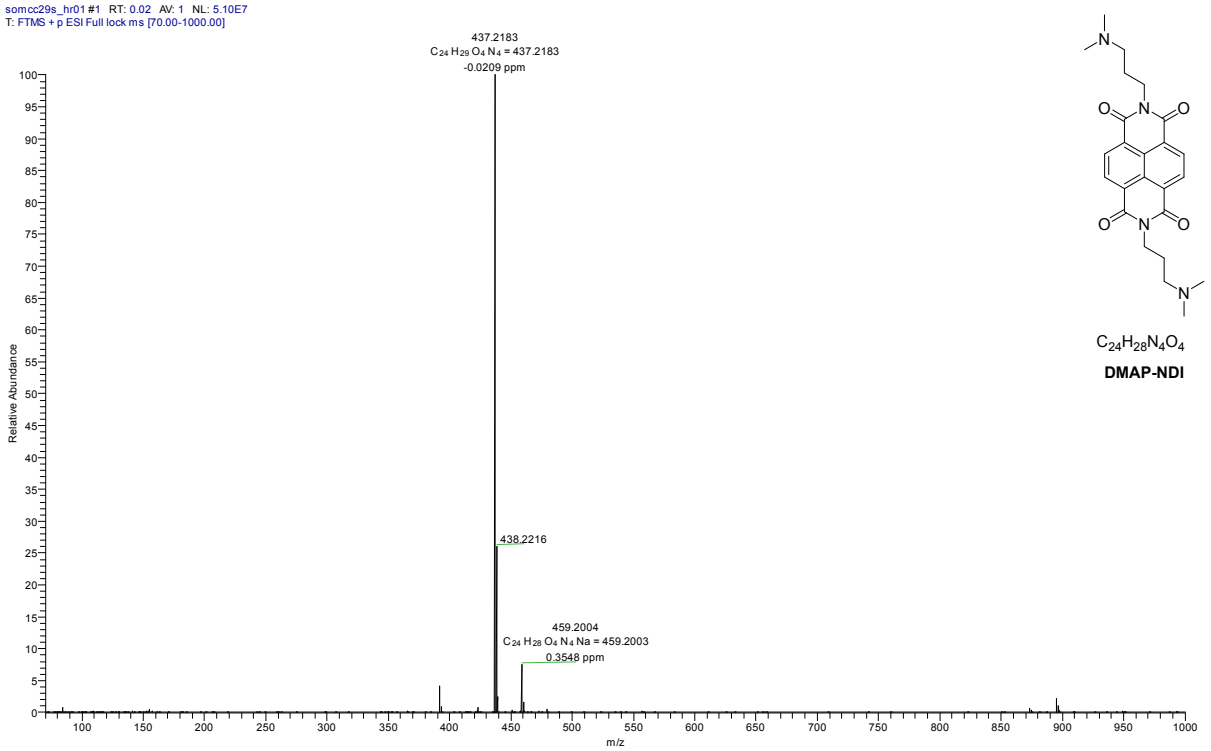


Figure S25. *MS (ESI, positive) of DMAP-NDI: m/z calc for [MH]⁺ $C_{24}H_{29}N_4O_4$: 437.2189, found: 437.2183.*

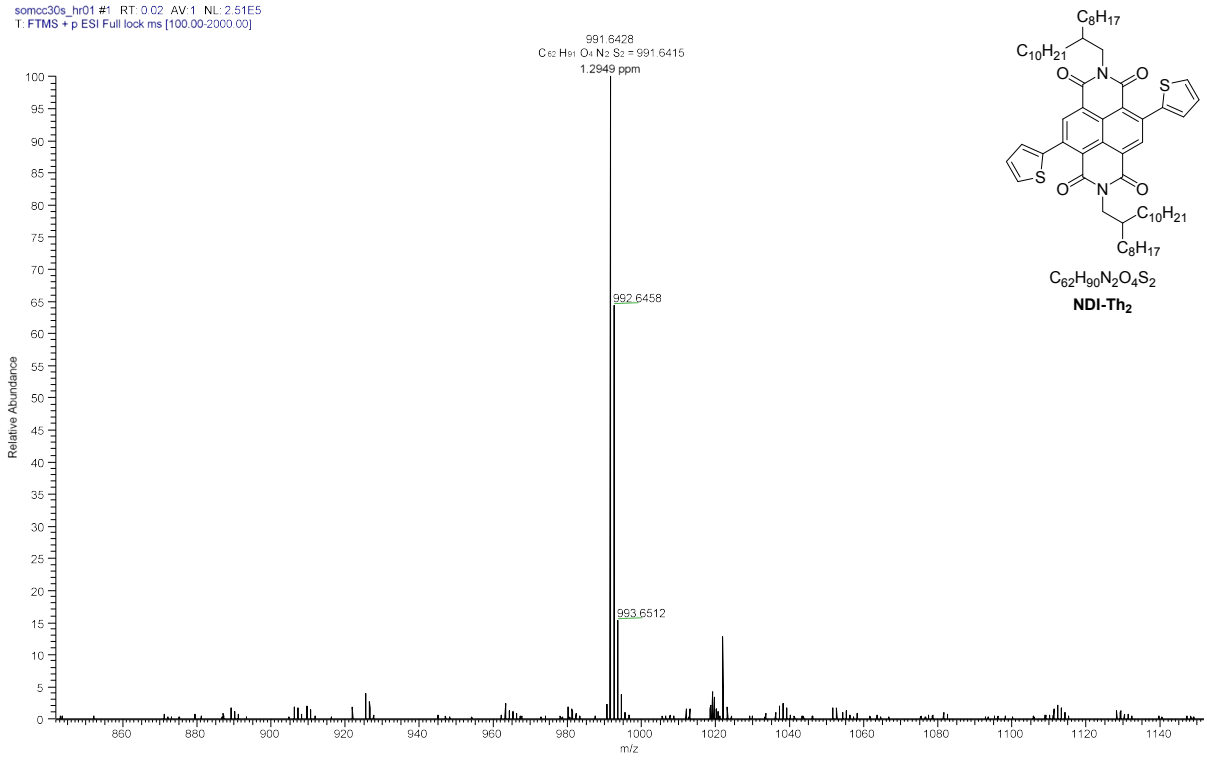


Figure S26. *MS (ESI, positive) of NDI-Th_2: m/z calc for [MH]⁺ $C_{62}H_{91}N_2O_4S_2$: 991.6420, found: 991.6428.*

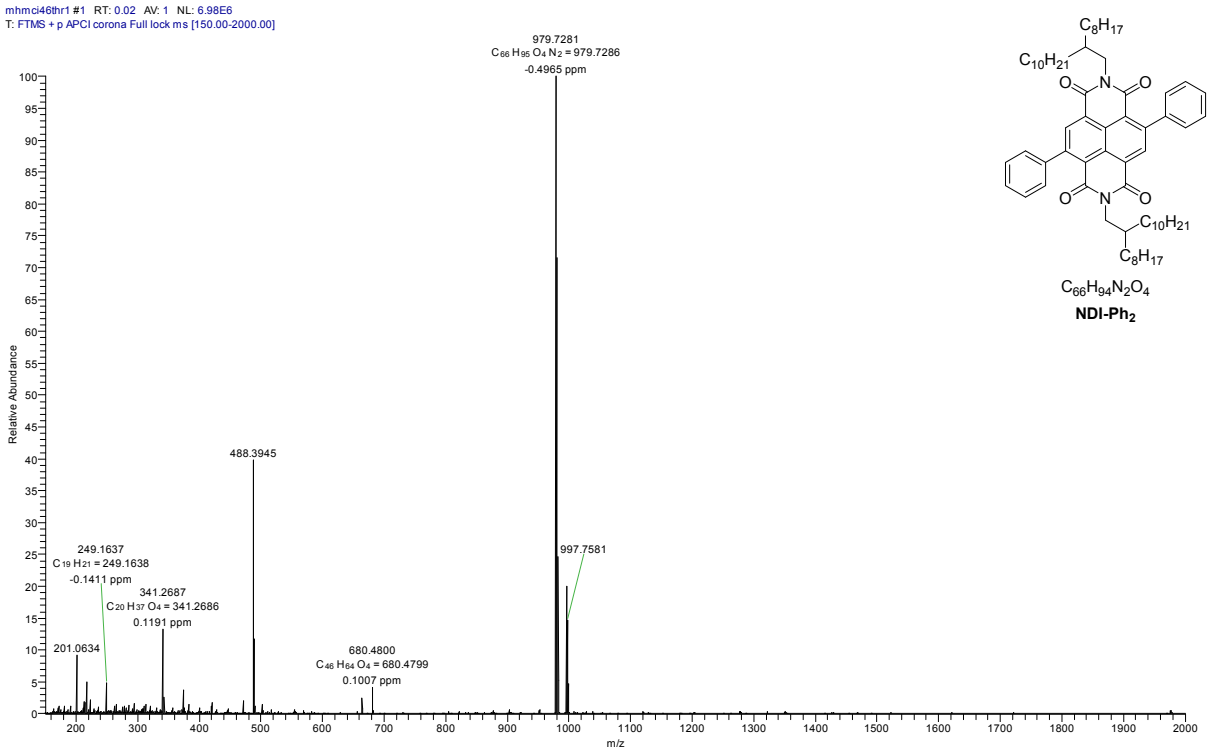


Figure S27. *MS (ESI, positive) of NDI-Ph$_2$: m/z calc for [MH]$^+$ $C_{66}H_{95}N_2O_4$: 979.7292, found: 979.7281, m/z calc for [MNH$_4$]$^+$ $C_{66}H_{99}N_3O_4$: 997.7636, found: 997.7581.*

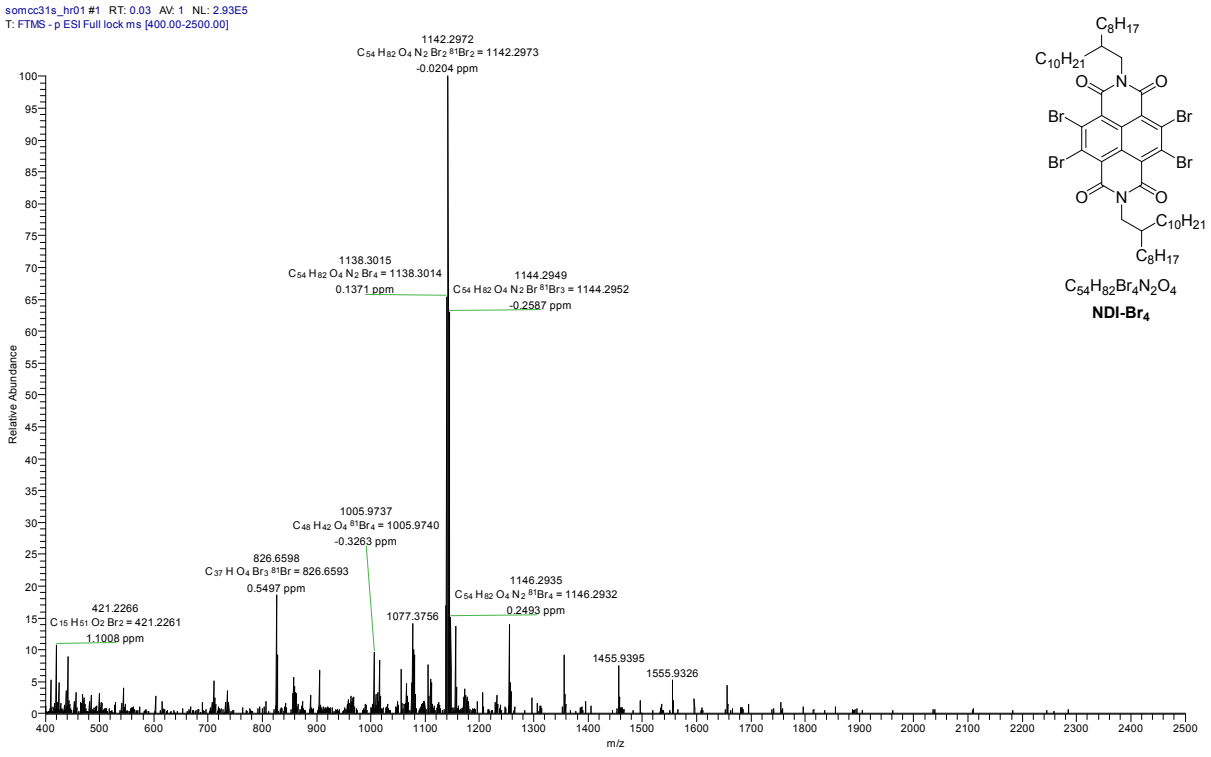


Figure S28. *MS (ESI, negative) of NDI-Br$_4$: m/z calc for [M]$^-$ $C_{54}H_{82}N_2O_4Br_4$: 1142.2967, found: 1142.2972.*

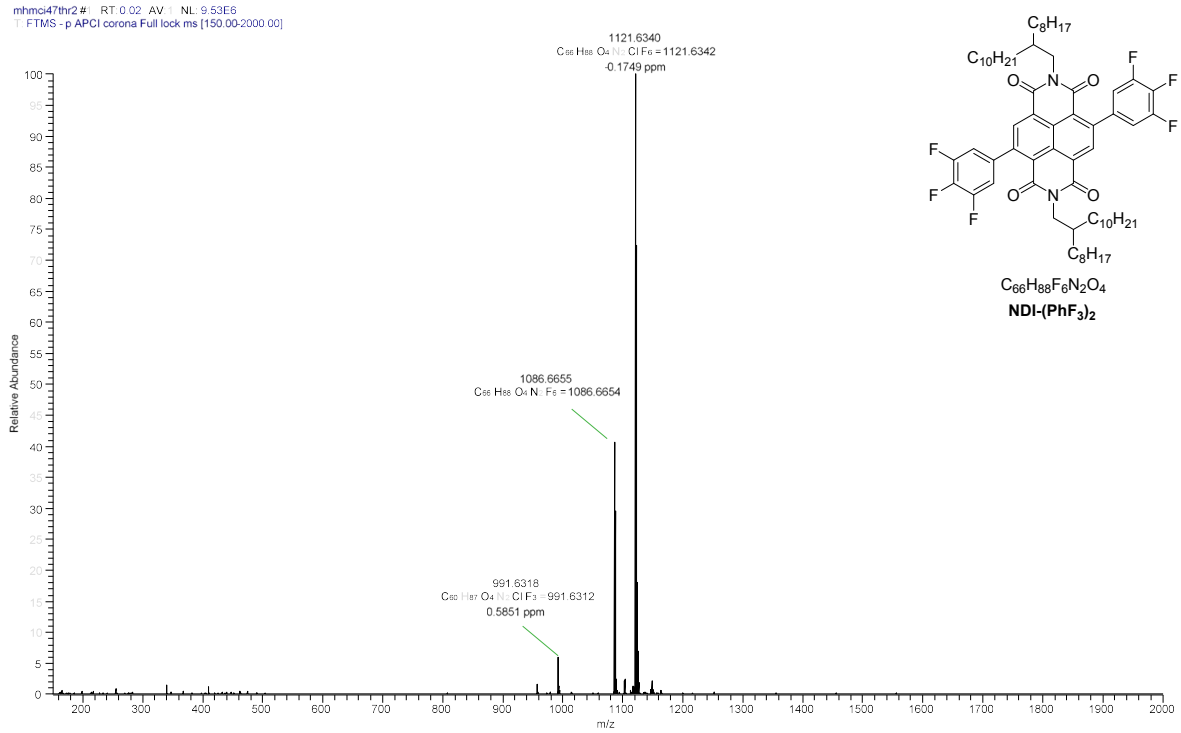


Figure S29. *MS (ESI, negative) of NDI-$(PhF_3)_2$: m/z calc for $[M]^-$ $C_{66}H_{85}F_6N_2O_4$: 1086.6648, found: 1086.6655, m/z calc. for $[MCl]^-$ $C_{66}H_{88}F_6N_2O_4Cl$: 1121.6337, found: 1121.6340.*

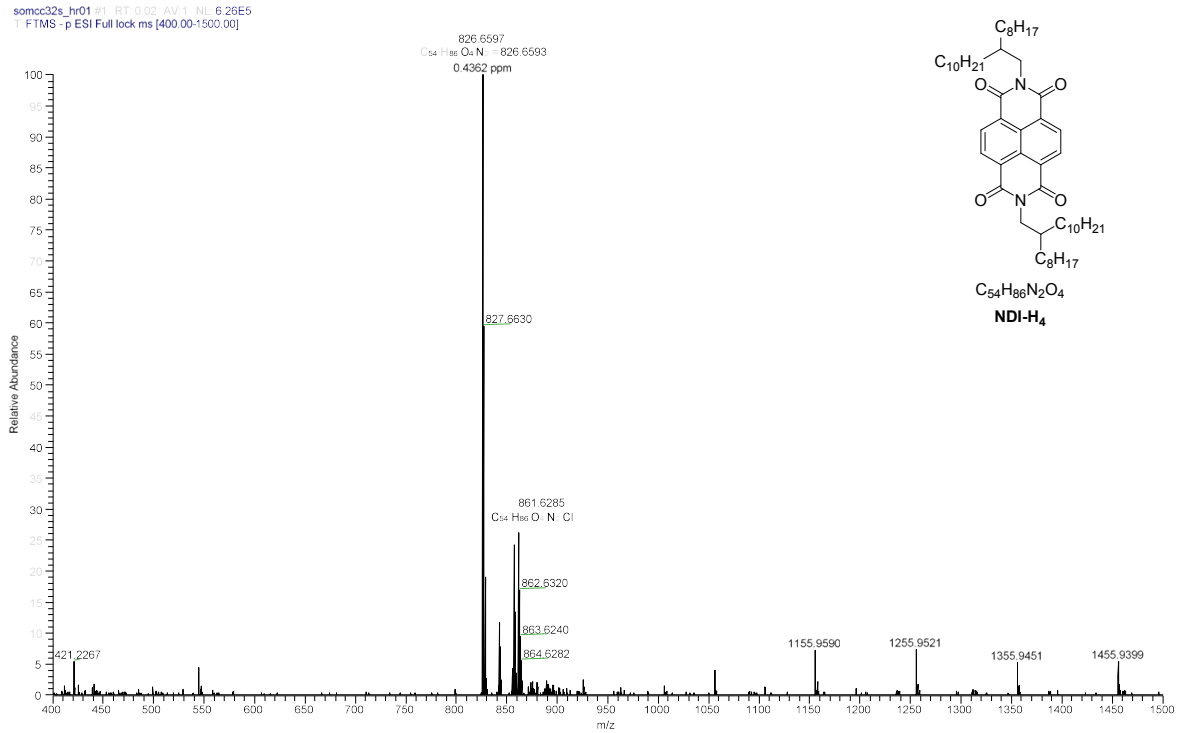


Figure S30. *MS (ESI, negative) of NDI-H_4: m/z calc for $[M]^-$ $C_{54}H_{86}N_2O_4$: 826.6588, found: 826.6597, m/z calc for $[MCl]^-$ $C_{54}H_{86}N_2O_4Cl$: 861.6276, found: 861.6285.*

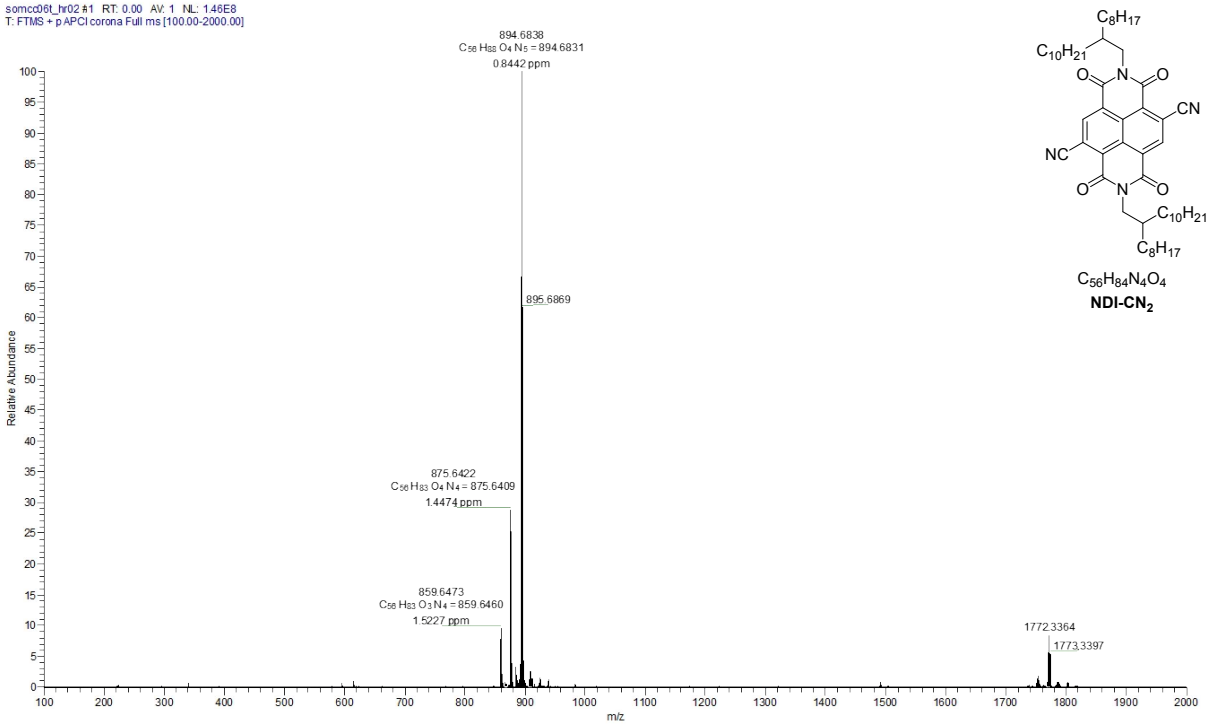


Figure S31. *MS (APCI, positive) of NDI-CN_2: m/z calc for $[MNH_4]^+$ $C_{56}H_{88}N_5O_4$: 894.6836, found: 894.6838.*