

Supporting Information

Monodisperse N-Doped Graphene Nanoribbons Reaching 7.7 Nanometers in Length

Diego Cortizo-Lacalle, Juan P. Mora-Fuentes, Karol Strutyński, Akinori Saeki, Manuel Melle-Franco, and Aurelio Mateo-Alonso**

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Results and Discussion

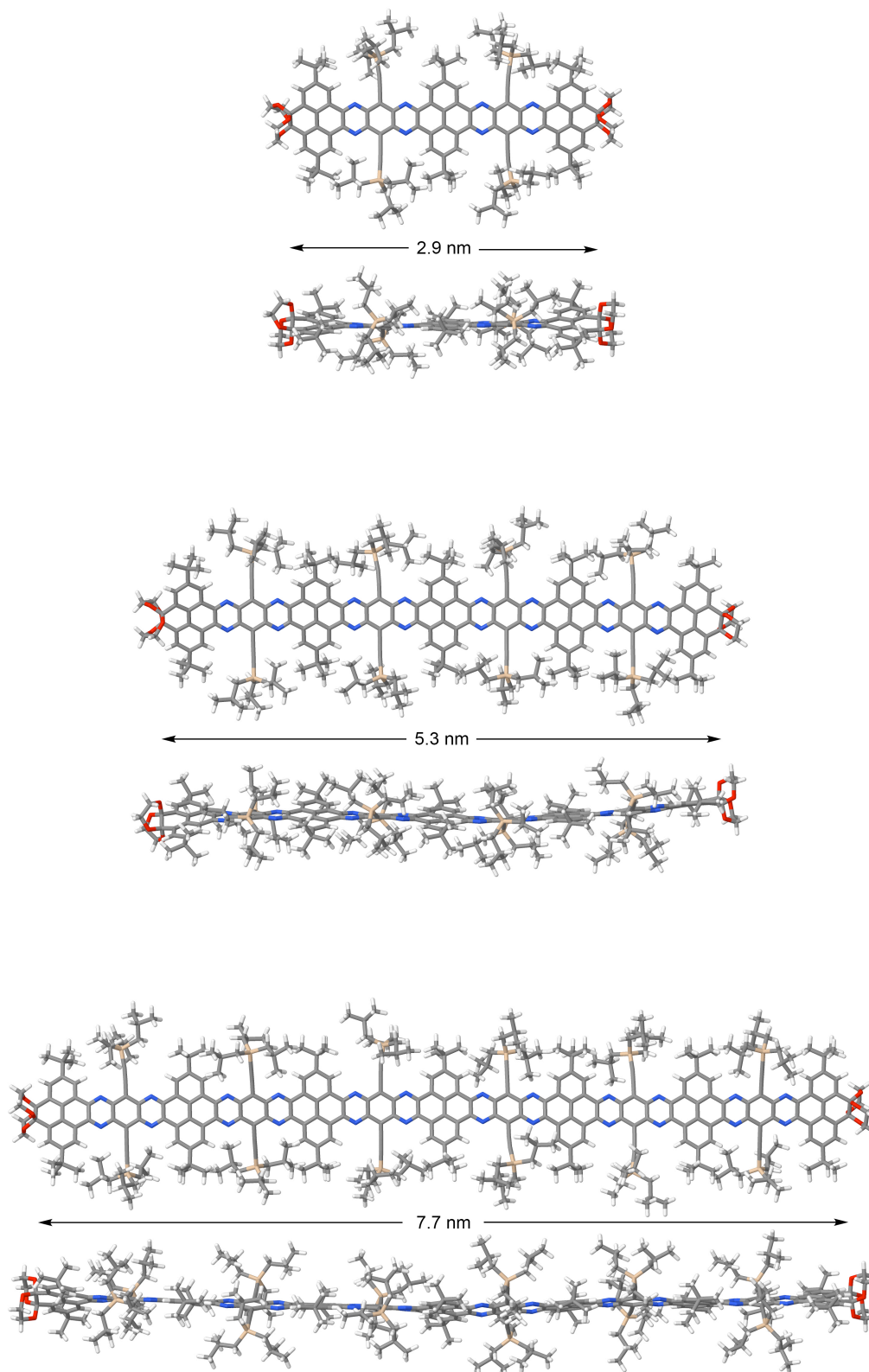


Figure S1. Structure and geometries of NR-10, NR-20 and NR-30 at the B3LYP 6-31g(d,p) level.

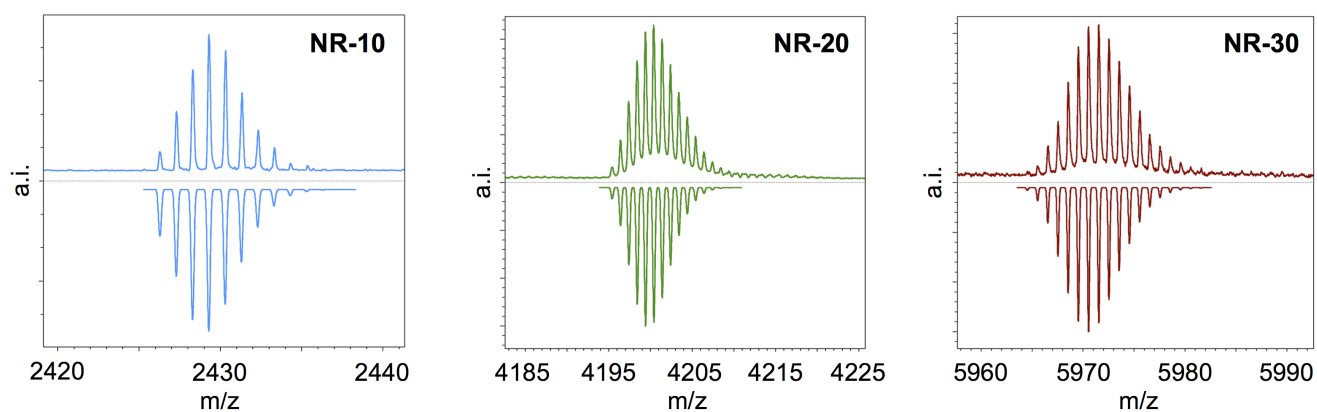


Figure S2. Experimental (top) and calculated (bottom) MALDI-TOF HRMS spectra.

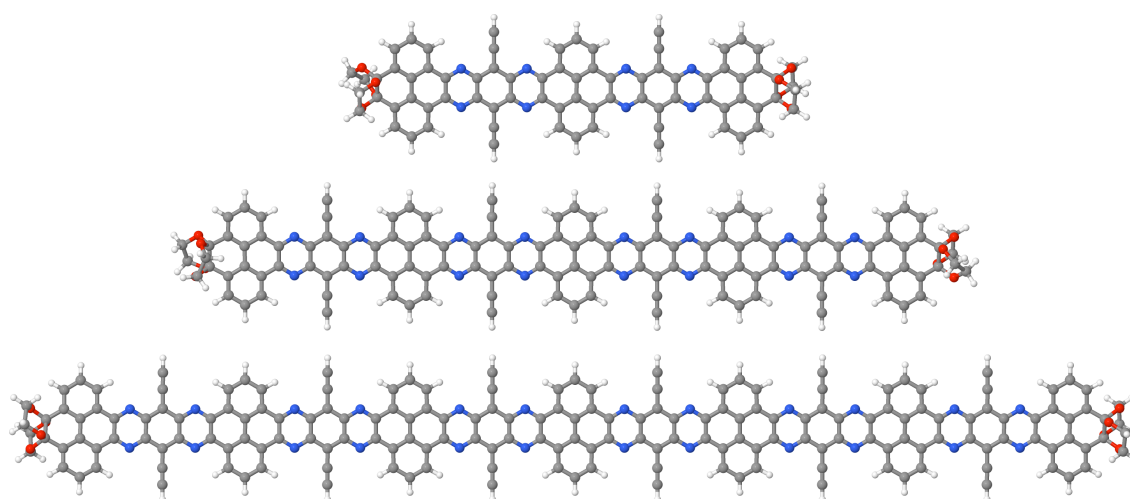


Figure S3. Structure and geometries of NR-10-H, NR-20-H and NR-30-H at the B3LYP 6-31g(d,p) level.

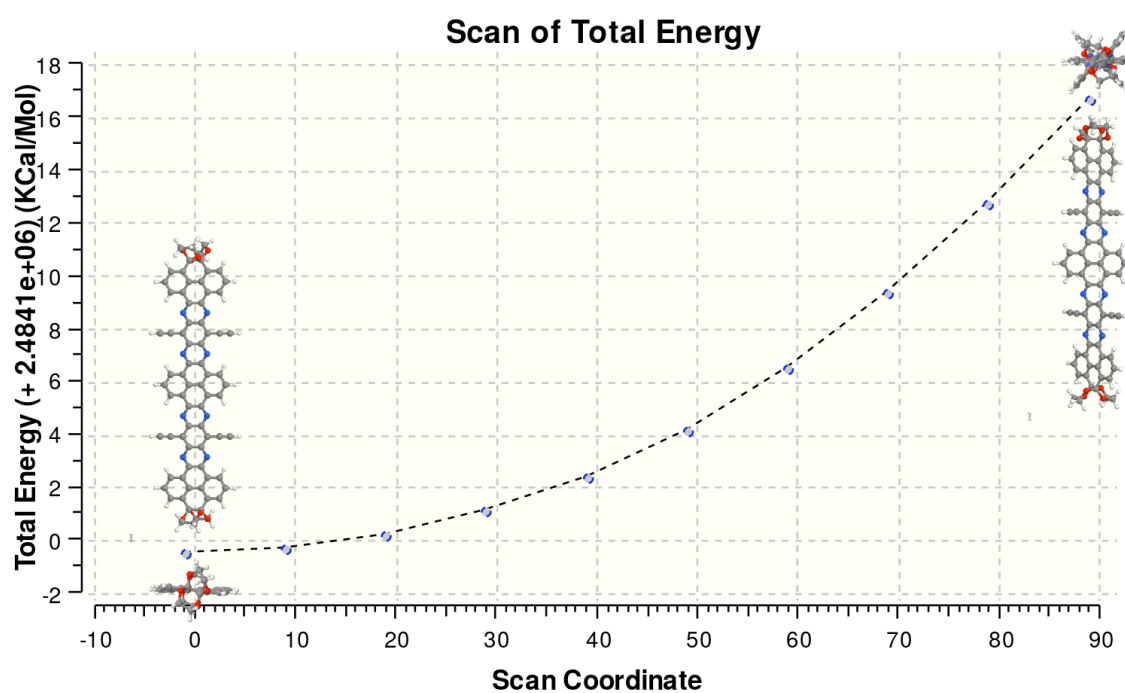


Figure S4. Distortion energy for NR-10-H at the B3LYP-6-31g(d,p) level in vacuum with different twisting angles from 0 to 90 degrees.

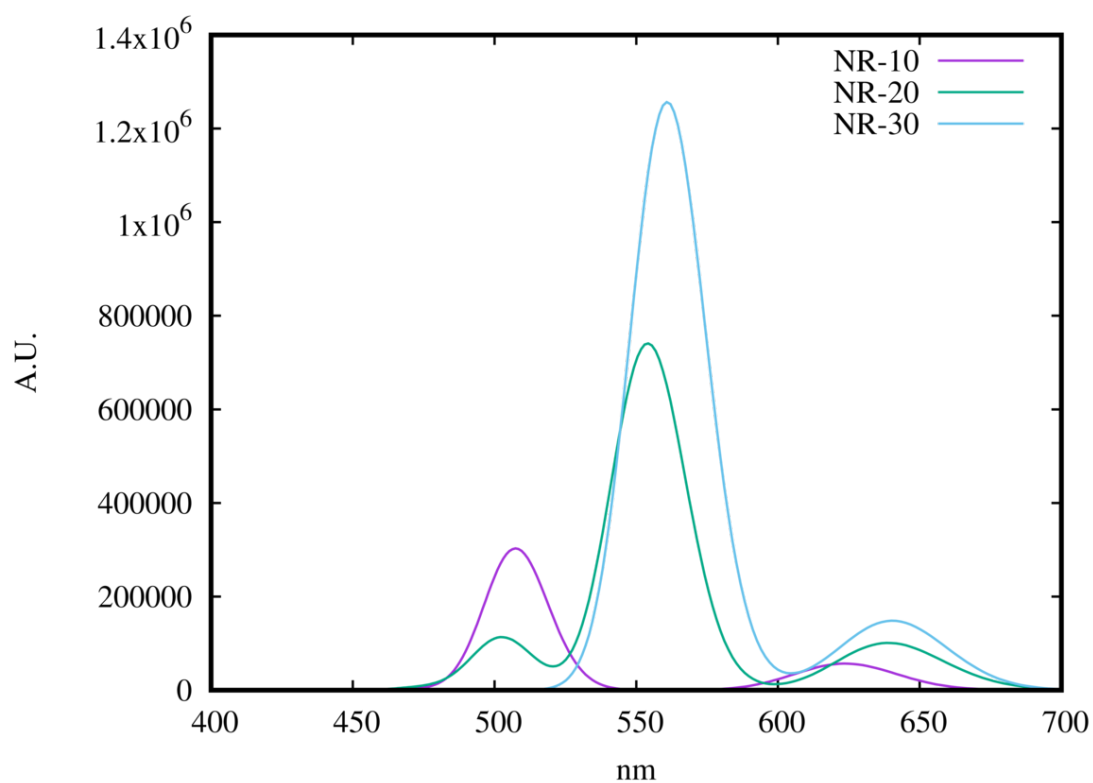


Figure S5. Absorption spectra for NR-10, NR-20 and NR-30 at the B3LYP-6-31g(d,p) level in vacuum.

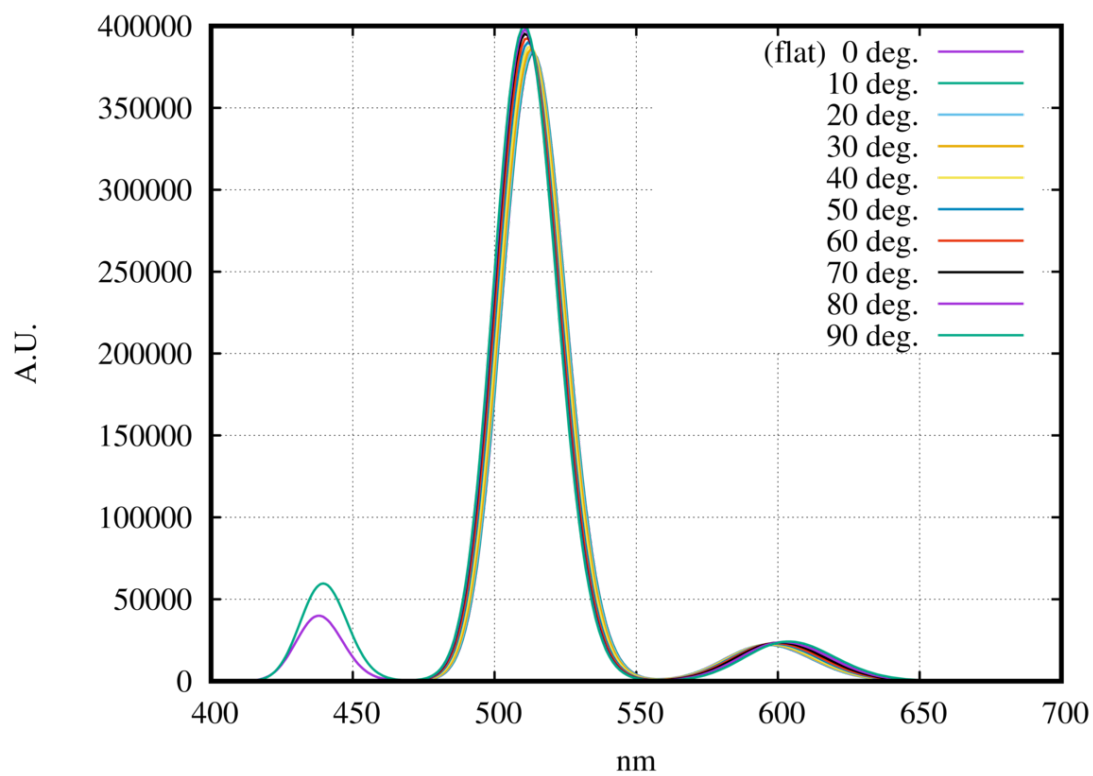


Figure S6. Absorption spectra for NR-10-H at the B3LYP-6-31g(d,p) level in vacuum with different twisting angles up to 90 degrees.

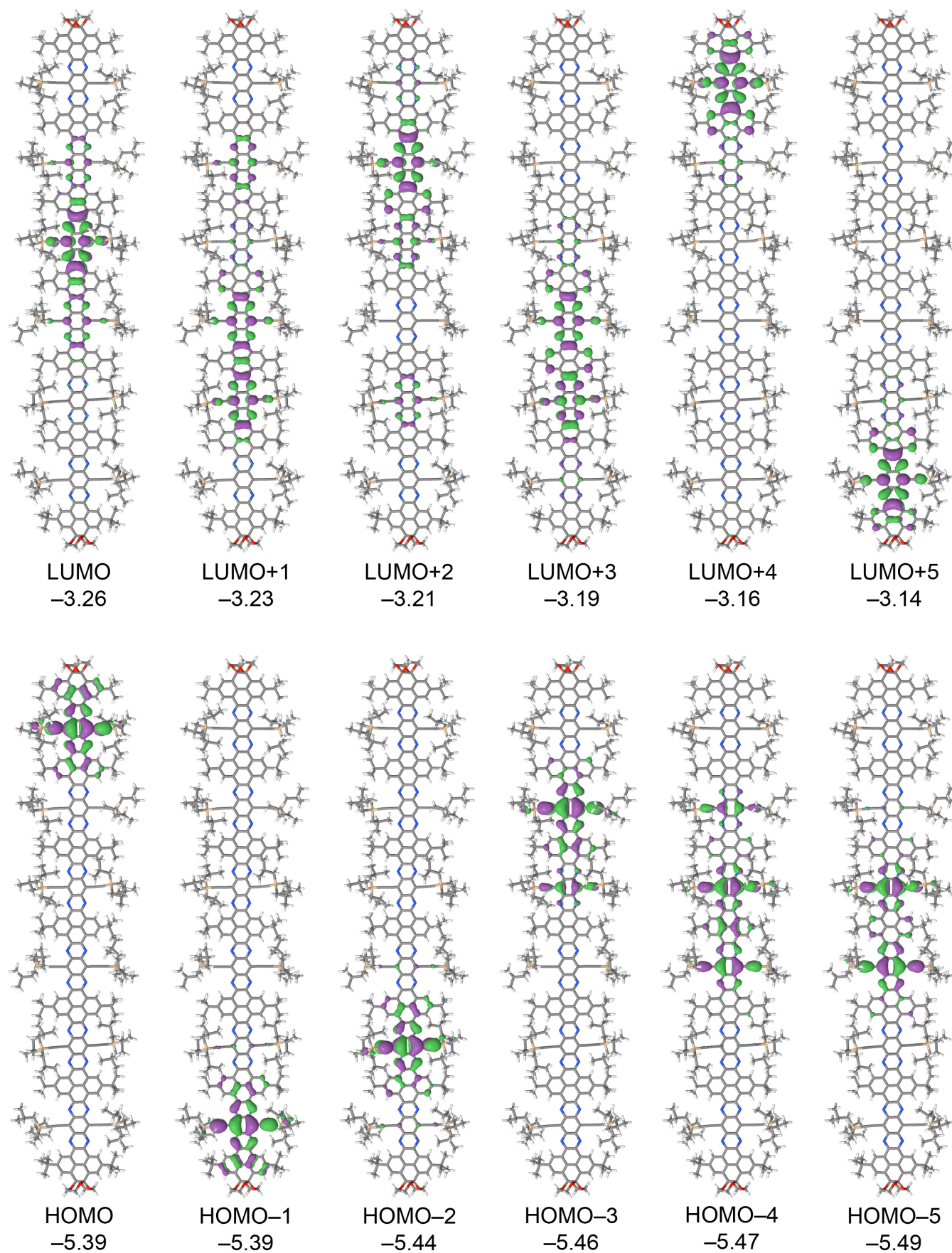


Figure S7. Frontier orbitals of NR-30 computed with the B3LYP Hamiltonian with the 6-31g(d,p) basis set in vacuum. Energy values given in eV.

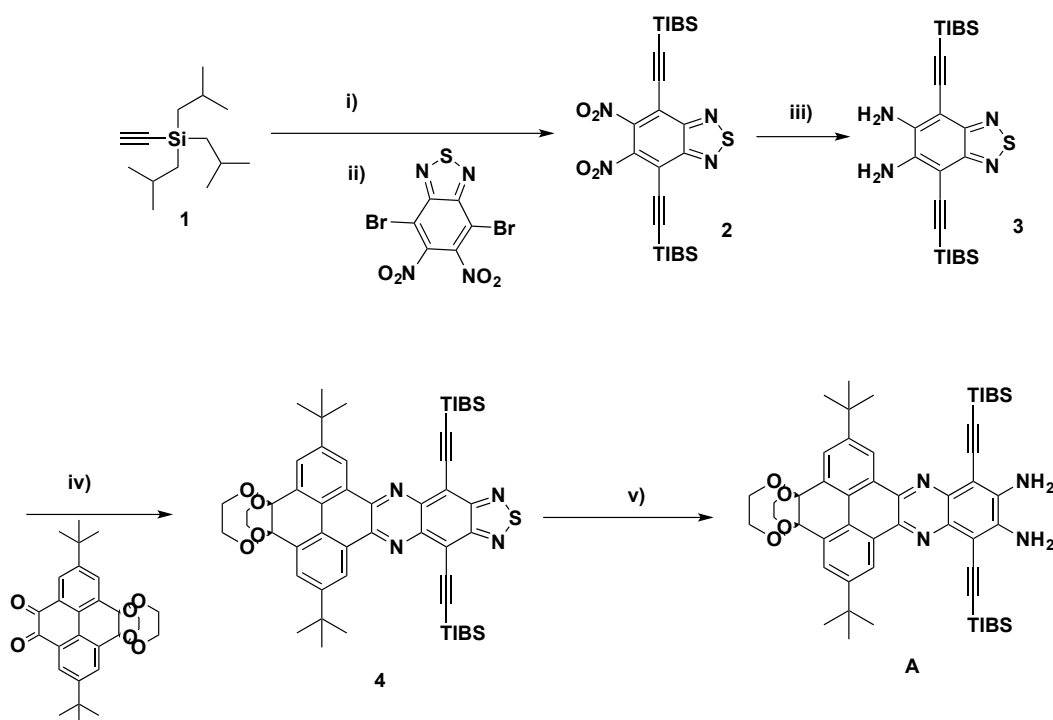
Table S1. Frontier orbitals computed with the B3LYP Hamiltonian with the 6-31g(d,p) basis set in vacuum for all geometries and the 6-311+g(2d,p) basis set in CH₂Cl₂ for the NR-H series. All geometries were optimized at the B3LYP-6-31g(d,p) level. The colour code is: LUMOs, HOMOs and gaps. All values in eV.

NR Series B3LYP 6-31g(d,p)																			gap
10	-0.95	-0.98	-0.99	-1.31	-1.57	-1.63	-1.64	-3.07	-3.12	-5.35	-5.38	-5.96	-6.00	-6.05	-6.21	-6.34	-6.51	2.23	
20	-1.63	-1.67	-1.70	-1.76	-1.80	-3.10	-3.12	-3.19	-3.23	-5.36	-5.38	-5.43	-5.45	-5.87	-5.94	-5.96	-5.99	2.13	
30	-1.77	-1.79	-1.84	-3.14	-3.16	-3.19	-3.21	-3.23	-3.26	-5.39	-5.39	-5.44	-5.46	-5.47	-5.49	-5.88	-5.93	2.13	
NR-H Series B3LYP 6-31g(d,p)																			
10	-1.05	-1.16	-1.18	-1.38	-1.68	-1.74	-1.74	-3.17	-3.21	-5.55	-5.56	-6.01	-6.23	-6.25	-6.36	-6.53	-6.58	2.34	
20	-1.75	-1.78	-1.81	-1.86	-1.90	-3.21	-3.24	-3.28	-3.32	-5.58	-5.61	-5.66	-5.67	-6.00	-6.11	-6.25	-6.31	2.26	
30	-1.88	-1.89	-1.94	-3.23	-3.23	-3.29	-3.30	-3.32	-3.35	-5.60	-5.60	-5.67	-5.67	-5.68	-5.69	-6.00	-6.05	2.25	
NR-H Series B3LYP 6-311+g(2d,p) CH ₂ Cl ₂																			
10	-1.56	-1.77	-1.56	-1.77	-2.08	-2.11	-2.19	-3.62	-3.64	-5.99	-6.00	-6.30	-6.52	-6.54	-6.66			2.35	
20	-2.19	-2.20	-2.19	-2.20	-2.26	-3.63	-3.63	-3.66	-3.69	-6.00	-6.00	-6.03	-6.05	-6.24	-6.37			2.31	
30			-2.28	-3.63	-3.63	-3.66	-3.67	-3.68	-3.69	-6.00	-6.00	-6.03	-6.03	-6.04	-6.05			2.31	

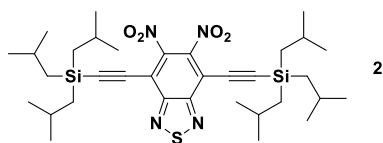
Experimental Procedures

Synthesis and characterisation

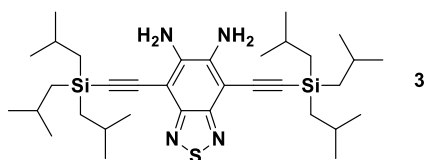
Commercial chemicals and solvents were used as received. Tetrahydrofuran was dried using an Innovative Pure Solve solvent purification system. Analytical thin layer chromatography (TLC) was carried out using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck. Column chromatography was carried out using Silica gel 60 (40-60 μm) from Scharlab. NMR spectra in solution were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometer at 298 K using partially deuterated solvents as internal standards. High Resolution Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) Mass Spectrometry experiments were recorded in Biomagune in a Ultraflex III (Bruker Daltonics) MALDI-ToF (frequency-tripled (355 nm) Nd:YAG laser) by Dr. Javier Calvo. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments MALDI-TOF) were recorded on Bruker REFLEX spectrometer in POLYMAT by Dr. Antonio Veloso.



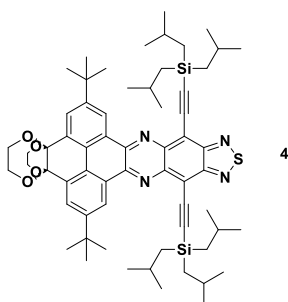
Scheme S1. Synthesis of A. Reaction conditions: *i)* $n\text{BuLi}$ (1.6 M), dry THF, -78°C , 45 min., Bu_3SnCl , -78°C , r.t overnight; *ii)* 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, dry THF, reflux, 48 h; *iii)* iron, nitrogen atmosphere, 55°C , 4h; *iv)* 2,7-di-*tert*-butyl-10,11-dihydro-8b,12a-(epoxyethanoxy)pyreno[4,5-b][1,4]dioxine-4,5-dione, $\text{CHCl}_3:\text{AcOH}$ (5:3), reflux, 48 h; *v)* LiAlH_4 , dry diethyl ether, 0°C to room temperature, overnight.

5,6-dinitro-4,7-bis((triisobutylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole, 2

Ethynyltriisobutylsilane^[1] (8.42 g, 37.5 mmol) was dissolved in dry THF (80 mL) and the reaction was cooled to -78 °C. ⁿBuLi (26.9 mL, 1.6 M in hexanes) was slowly added and the reaction was stirred for 1 hour. Tributyltin chloride (17.4 g, 52.51 mmol) was slowly added to the reaction and the reaction was stirred overnight at room temperature. NH₄Cl (aq.) was added and the product was extracted with diethyl ether (3x 30 mL). The oil was used in the next step without further purification. The oil was dissolved in dry THF (20 mL) and added to a solution of 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole^[2] (4.0 gr, 10.4 mmol) and Pd(PPh₃)₂Cl₂ (0.71 g, 1.02 mmol) in dry THF (120 mL). The reaction was refluxed for 48 hours under nitrogen. The reaction was cooled down to room temperature and water was added. The product was extracted with chloroform (3 x 100 mL), dried over sodium sulfate and the organic phase was removed by rotary evaporation. The resulting solids were loaded onto a chromatographic column (eluent mixture hexane:dichloromethane 6:1). The product was isolated as a yellow solid (4.6 g, 66%). ¹H-NMR (CDCl₃): 2.05-1.88 (6 H, m), 1.04 (36 H, *J* = 8.0 Hz, d) and 0.80 (12 H, *J* = 8.0 Hz, d). ¹³C-NMR (CDCl₃): 153.18, 145.74, 117.79, 112.63, 94.78, 26.41, 25.22 and 24.62. MS (MALDI, pos.) (*m/z*): [M+Na]⁺ calcd. for C₃₄H₅₄NaN₄O₄SSi₂: 693.330; found 693.581.

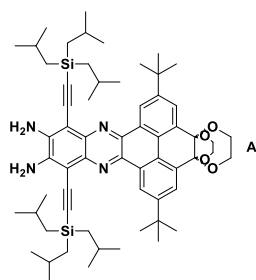
4,7-bis((triisobutylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole-5,6-diamine, 3

5,6-dinitro-4,7-bis((triisobutylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole (2.80 g, 4.2 mmol) was suspended in acetic acid, the mixture was bubbled with nitrogen for 15 minutes and iron (2.33 g, 42.0 mmol) was added. The reaction was stirred at 56°C for 5 hours. The reaction was cooled down to room temperature and water was added. The product was extracted with chloroform (3 x 100 mL), dried over sodium sulfate and the organic phase was removed by rotary evaporation. The resulting solids were loaded onto a chromatographic column (eluent mixture hexane:dichloromethane 4:1). The product was isolated as a bright yellow solid (1.1 g, 43%). ¹H-NMR (CDCl₃): 4.85 (4H, s), 2.06-1.89 (6 H, m), 1.05 (36 H, *J* = 8.0 Hz, d) and 0.80 (12 H, *J* = 8.0 Hz, d). ¹³C-NMR (CDCl₃): 150.50, 143.53, 106.51, 99.41, 97.31, 26.55, 25.34 and 25.23. MS (MALDI, pos.) (*m/z*): [M+Na]⁺ calcd. for C₃₄H₅₈NaN₄SSi₂: 633.382; found 633.462.

Synthesis of 4

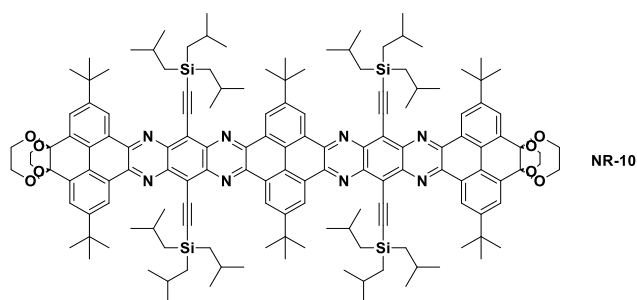
2,7-di-tert-butyl-10,11-dihydro-8b,12a-(epoxyethanoxy)pyreno[4,5-b][1,4]dioxine-4,5-dione^[3] (357 mg, 0.825 mmol) and compound **3** (637 mg, 1.042 mmol) were dissolved in chloroform (5 mL) and acetic acid (3 mL), and the reaction was refluxed for 48 hours. The reaction was cooled to room temperature and water was added. The product was extracted with chloroform (3 x 20 mL), dried over magnesium sulfate and eliminated by rotary evaporation. The solids were loaded onto a chromatographic column (eluent mixture hexane:dichloromethane 4:1) to obtain the product as a dark red solid (542 mg, 63%). ¹H-NMR (CDCl₃): 9.47 (2H, *J* = 4.0 Hz, d), 8.19 (2H, *J* = 4.0 Hz, d), 4.37 (4H, *br s*), 3.85 (4H, *br s*), 2.21-2.05 (6H, m), 1.61 (18H, s), 1.13 (36H, *J* = 8.0 Hz, d) and 0.98 (12H, *J* = 8.0 Hz, d). ¹³C-NMR (CDCl₃): 155.00, 152.10, 145.32, 141.66, 132.72, 129.57, 127.39, 126.67, 124.84, 114.28, 112.78, 101.74, 93.49, 61.87, 35.61, 31.77, 26.69, 25.33 and 25.29. MS (MALDI, pos.) (*m/z*): [M]⁺ calcd. for C₆₂H₈₄N₄O₄SSi₂: 1036.575; found: 1036.545.

Synthesis of A



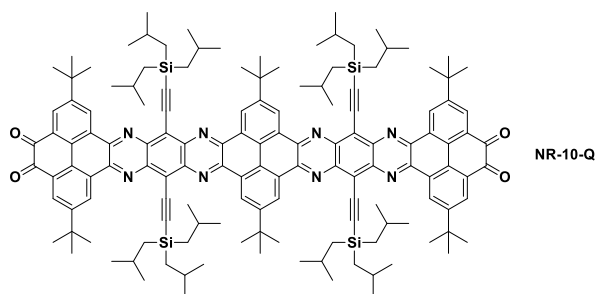
Compound **4** (170 mg, 0.164 mmol) was dissolved in dry diethyl ether (24 mL) and cooled down to 0°C. LiAlH₄ (60 mg, 9 eq.) was added portionwise and the reaction was stirred at room temperature overnight. The reaction was quenched with NH₄Cl (aq.) and the product was extracted with ethyl acetate. The organic phase was dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The solids were loaded onto a chromatographic column (eluent mixture dichloromethane:hexane 1:1). The product was isolated as a bright yellow solid (156 mg, 94%). ¹H-NMR (CDCl₃): 9.46 (2H, *J* = 4.0 Hz, d), 8.12 (2H, *J* = 4.0 Hz, d), 4.79 (4H, s), 4.36 (4H, *br s*), 3.85(4H, *br s*), 2.10-1.95 (6H, m), 1.59 (18H, s), 1.09 (36H, *J* = 8.0 Hz, d) and 0.91 (12H, *J* = 8.0 Hz, d). ¹³C-NMR (CDCl₃): 150.88, 142.89, 140.03, 138.98, 131.96, 130.34, 125.68, 124.11, 123.13, 106.61, 104.04, 101.04, 93.98, 61.96, 35.39, 31.45, 26.67 and 25.43. MS (MALDI, pos.) (*m/z*): [M+H]⁺ calcd. for C₆₂H₈₉N₄O₄Si₂: 1009.642; found: 1009.988.

Synthesis of NR-10



Compound **A** (160 mg, 0.158 mmol) and compound **B**^[4] (24 mg, 0.064 mmol) were dissolved in chloroform and acetic acid was added and the reaction was refluxed for 48 hours. Water was added and the product was extracted with chloroform (3x25). The organic phase was dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The resulting solids were precipitations repeatedly until the product was obtained pure as bright red-purple solid (130 mg, 87%). ¹H-NMR (CDCl₃): 10.04 (4H, s), 9.60 (4H, *J* = 2.0 Hz, d), 8.25 (4H, *J* = 2.0 Hz, d), 4.42 (8H, *br s*), 3.90 (8H, *br s*), 2.23-2.12 (12H, m), 1.92 (18H, s), 1.68 (36H, s) and 1.18-1.11 (96H, m). ¹³C-NMR (CDCl₃): 152.00, 151.44, 144.81, 144.72, 142.24, 132.58, 129.89, 129.78, 127.47, 127.37, 127.28, 126.45, 124.88, 122.00, 112.68, 102.64, 93.61, 61.93, 36.12, 35.71, 32.50, 31.96, 26.69, 25.45 and 25.35. HRMS (MALDI, pos.) (*m/z*): [M+Ag]⁺ calcd. for C₁₄₈H₁₉₀Ag₁N₈Si₄, 2429.2862; found, 2429.2981

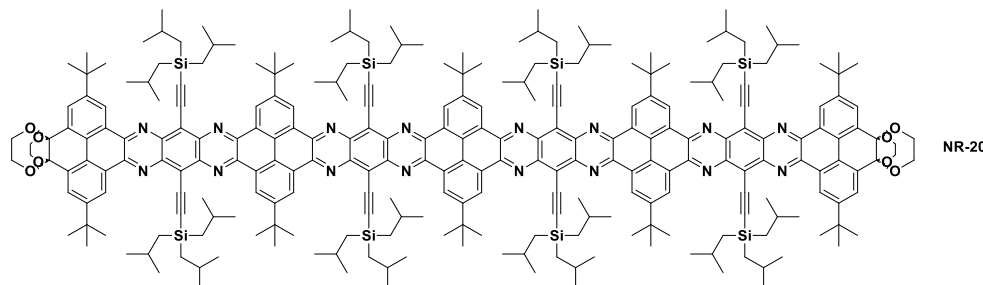
Synthesis of NR-10-Q



NR-10 (33 mg, 14 μmol) was dissolved in TFA (3 mL) and water was added. The reaction was stirred at room temperature and the reaction was followed by thin layer chromatography. Aqueous work-up was carried out and extracted with chloroform dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The solids were purified by chromatographic column (eluent 100% chloroform) and the product was isolated as a dark purple solid (26 mg, 86%). ¹H-NMR (CDCl₃): 10.01 (4H, s), 9.87 (4H, *J* = 4.0 Hz, d), 8.72 (4H, *J* = 4.0 Hz, d), 2.22-2.09 (12H, m), 1.89 (18H, s), 1.68 (36H, s) and 1.18-1.08 (96H, m). ¹³C-NMR (CDCl₃): 180.28,

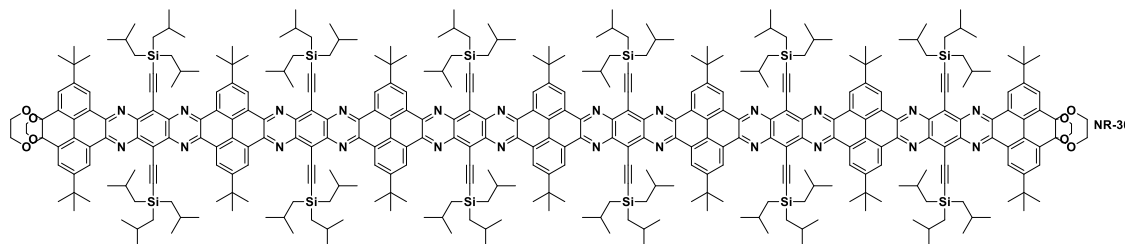
153.07, 151.71, 145.21, 143.39, 142.59, 142.12, 131.23, 130.60, 130.41, 129.71, 129.63, 127.76, 127.67, 122.34, 113.65, 102.36, 36.14, 35.86, 32.47, 31.68, 26.67, 25.45 and 25.34. MS (MALDI, pos.) (m/z): $[M]^+$ calcd. for $C_{140}H_{174}N_8O_4Si_4$: 2143.274; found: 2143.093.

Synthesis of NR-20



Compound **NR-10-Q** (26 mg, 12 μ mol) and Compound **A** (48 mg, 48 μ mol) were dissolved in chloroform and acetic acid was added and the reaction was refluxed for 4 days. Water was added and the product was extracted with chloroform (3x25). The organic phase was dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The resulting solids were precipitations repeatedly until the product was obtained pure as bright red-purple solid (42 mg, 87%). 1H -NMR ($CDCl_3$): 10.13-10.00 (12H, m), 9.60 (4H, s), 8.24 (4H, s), 4.41 (8H, *br s*), 3.90 (8H, *br s*), 2.26-2.13 (24H, m), 1.98-1.90 (54H, m), 1.68 (36H, s) and 1.23-1.11 (192H, m). ^{13}C -NMR ($CDCl_3$): 152.01, 151.54, 151.50, 144.99, 144.96, 144.80, 144.75, 142.46, 142.26, 132.59, 129.90, 129.83, 129.78, 127.52, 127.43, 127.29, 126.46, 124.90, 122.11, 122.02, 112.92, 112.71, 102.64, 93.62, 61.98, 36.15, 35.72, 32.53, 31.96, 26.73, 26.69, 25.50, 25.46, 25.40 and 25.36. HRMS (MALDI, pos.) (m/z): $[M+Ag]^+$ calcd. for $C_{264}H_{342}Ag_1N_{16}O_8Si_8$, 4200.4197; found 4200.3975.

Synthesis of NR-30



NR-20 (11 mg, 2.7 μ mol) was dissolved in TFA (1 mL) and water was added. The reaction was stirred at room temperature and the reaction was followed by thin layer chromatography. Aqueous work-up was carried out and extracted with chloroform dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The dark purple solids were filtrated through a silica plug and used in the next step without further purification. The dark purple solids obtained from the deprotection were dissolved in chloroform (3 mL) and acetic acid (1 mL) and compound **A** (13 mg, 12.8 μ mol, 4.8 eq.) were added. The reaction was refluxed for 3 days. The reaction mixture was diluted with chloroform and washed with water (3x25 mL). The organic phase was dried over sodium sulfate, filtrated and eliminated by rotary evaporation. The solids were loaded onto a chromatographic column (eluent mixture chloroform:hexane 9:1). The product was isolated as a bright pink solid (4 mg, 25% for the last two steps) 1H -NMR ($CDCl_3$): 10.17-9.96 (20H, m), 9.60 (4H, $J = 1.0$ Hz, s), 8.25 (4H, $J = 1.0$ Hz, s), 4.41 (8H, *br s*), 3.90 (8H, *br s*), 2.29-2.13 (36H, m), 1.98-1.90 (90H, m), 1.68 (36H, s) and 1.23-1.11 (288H, m). ^{13}C -NMR ($CDCl_3$): 152.01, 151.55, 151.49, 144.98, 144.97, 144.79, 144.74, 142.46, 142.25, 132.58, 129.89, 129.82, 129.76, 127.56, 127.52, 127.47, 127.28, 126.46, 124.90, 122.12, 122.10, 122.01, 112.93, 112.70, 102.63, 93.61, 36.16, 36.14, 35.71, 32.54, 32.52, 31.96, 29.86, 26.72, 26.69, 25.50, 25.45, 25.39, 25.35. HRMS (MALDI, pos.) (m/z): $[M+Ag]^+$ calcd. for $C_{380}H_{494}Ag_1N_{24}O_8Si_{12}$, 5970.5377; found 5970.5474.

Steady-state electronic absorption

Absorption spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer.

Photoluminescence

Photoluminescence spectra were recorded on a LS55 Perkin-Elmer Fluorescence spectrometer.

Electrochemistry

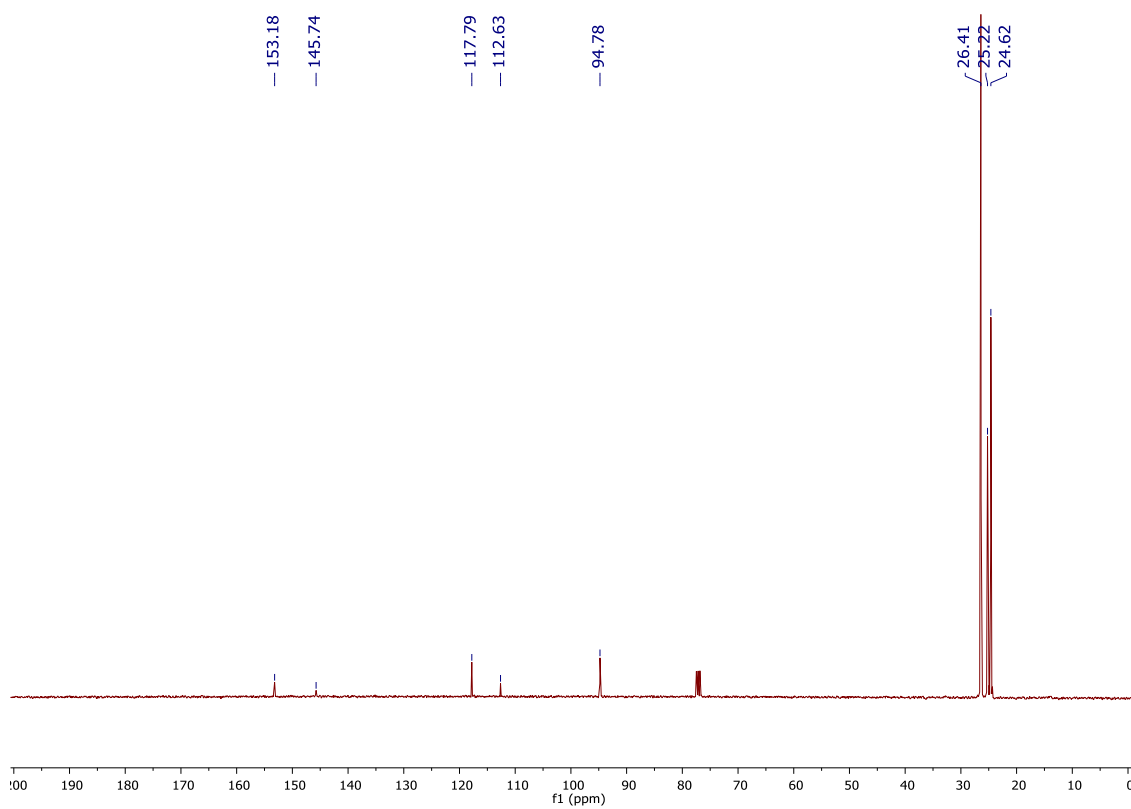
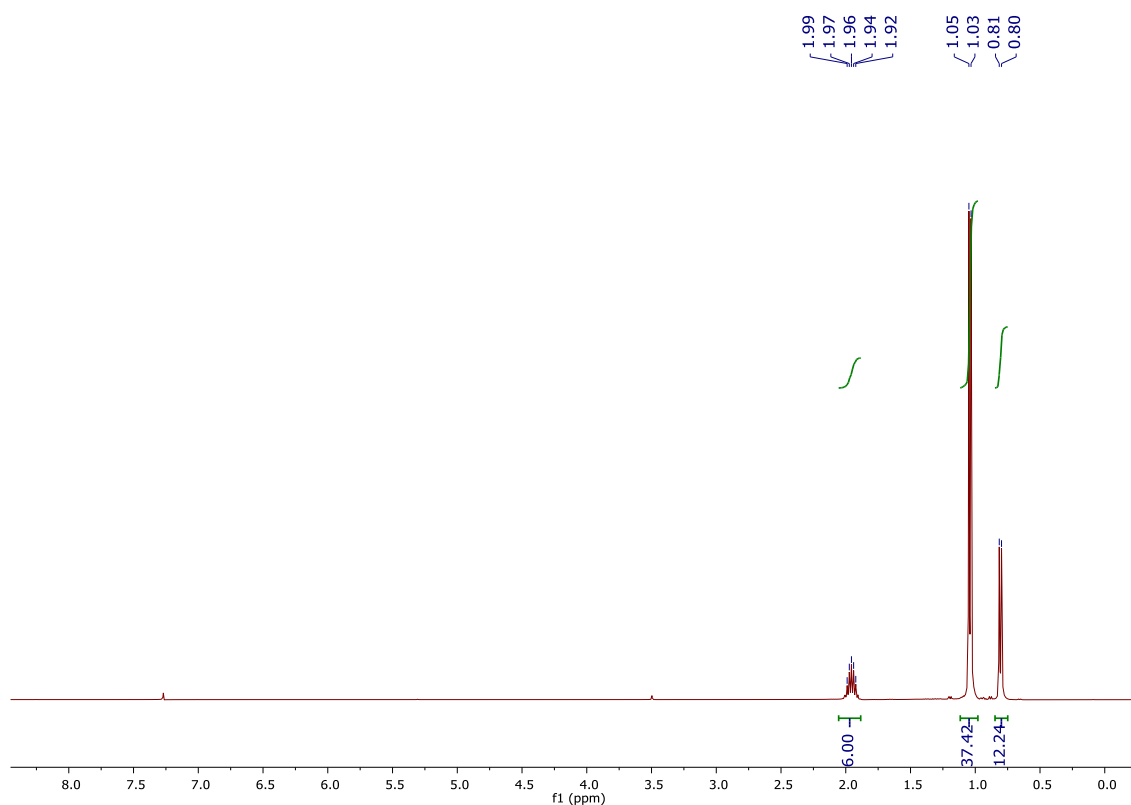
Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with glassy carbon disc working electrode, a platinum wire counter electrode and a silver wire pseudoreference electrode. All the potential values are reported versus the redox potential of the ferrocene/ferrocenium couple.

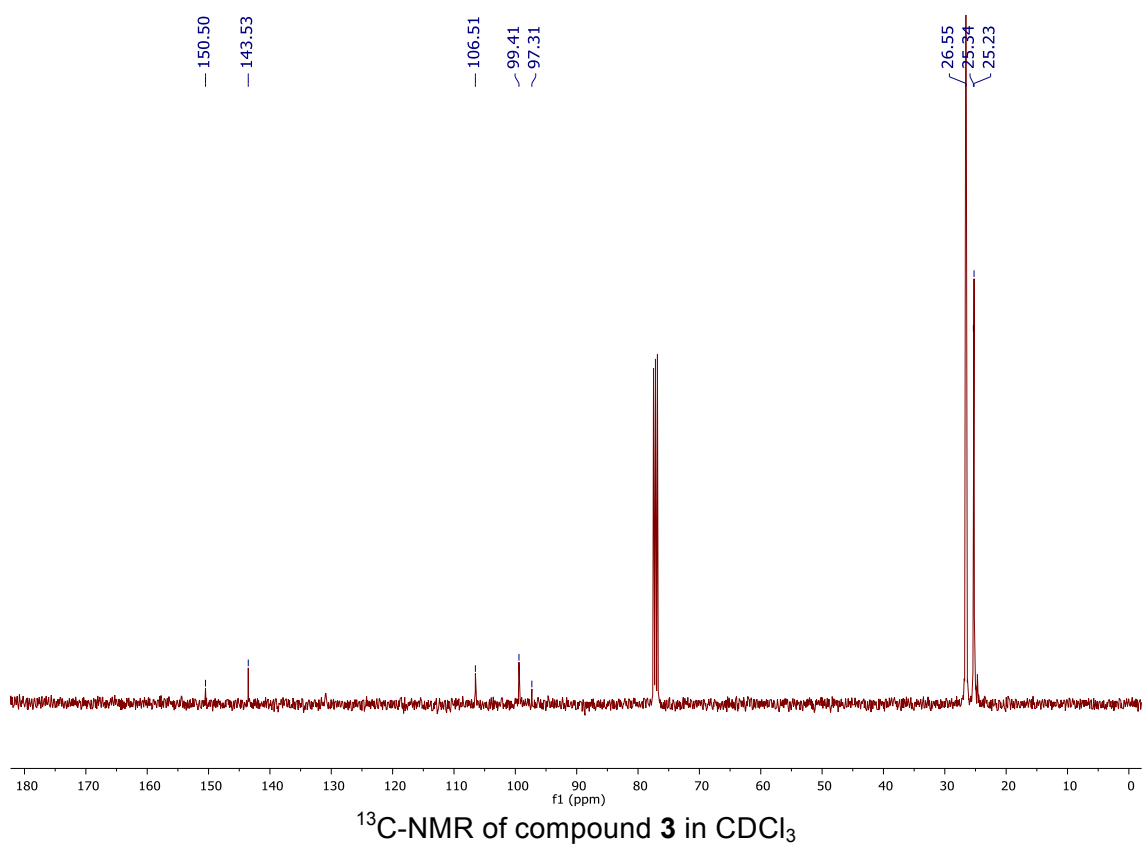
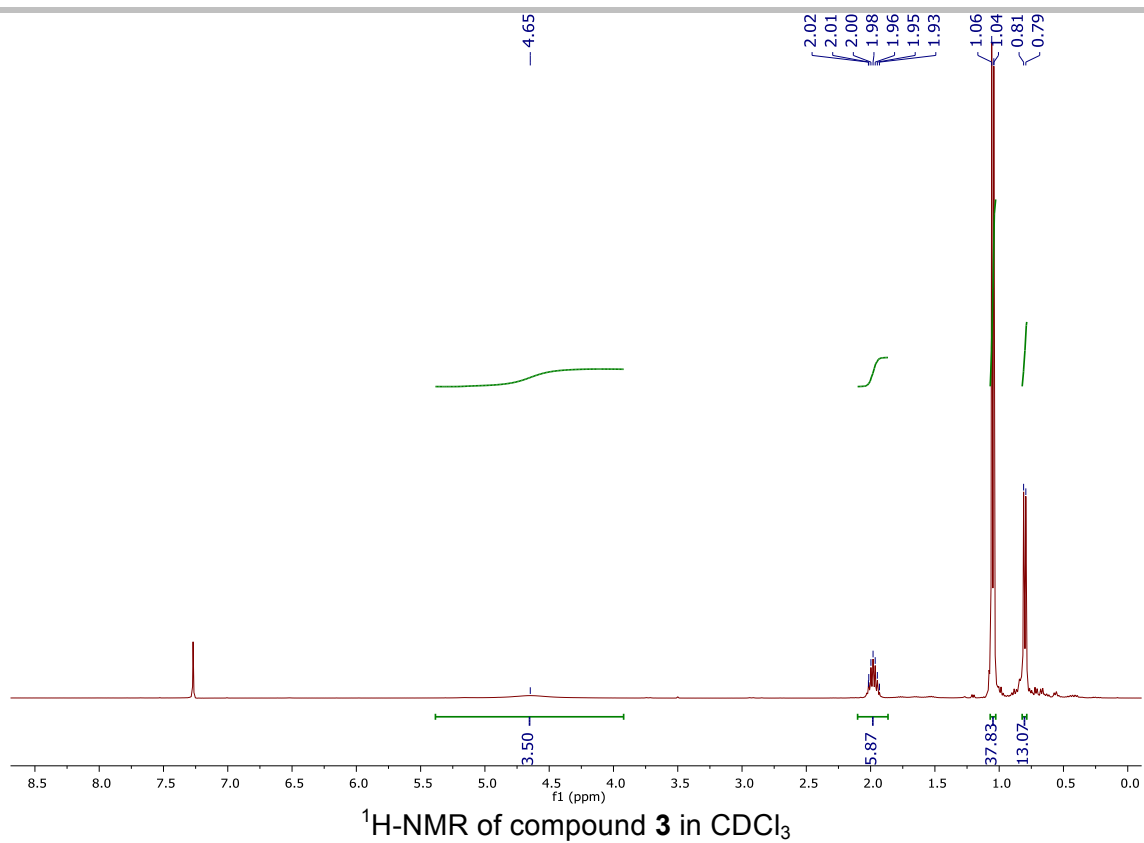
Calculations

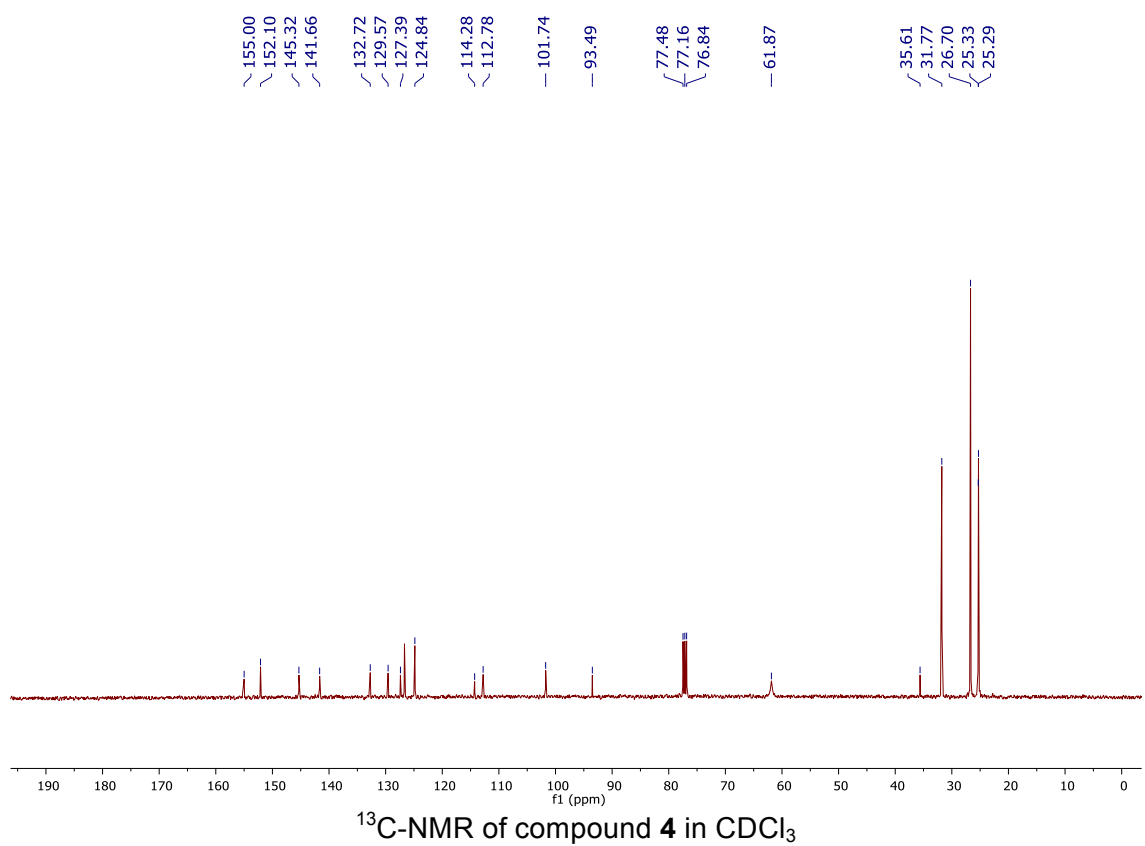
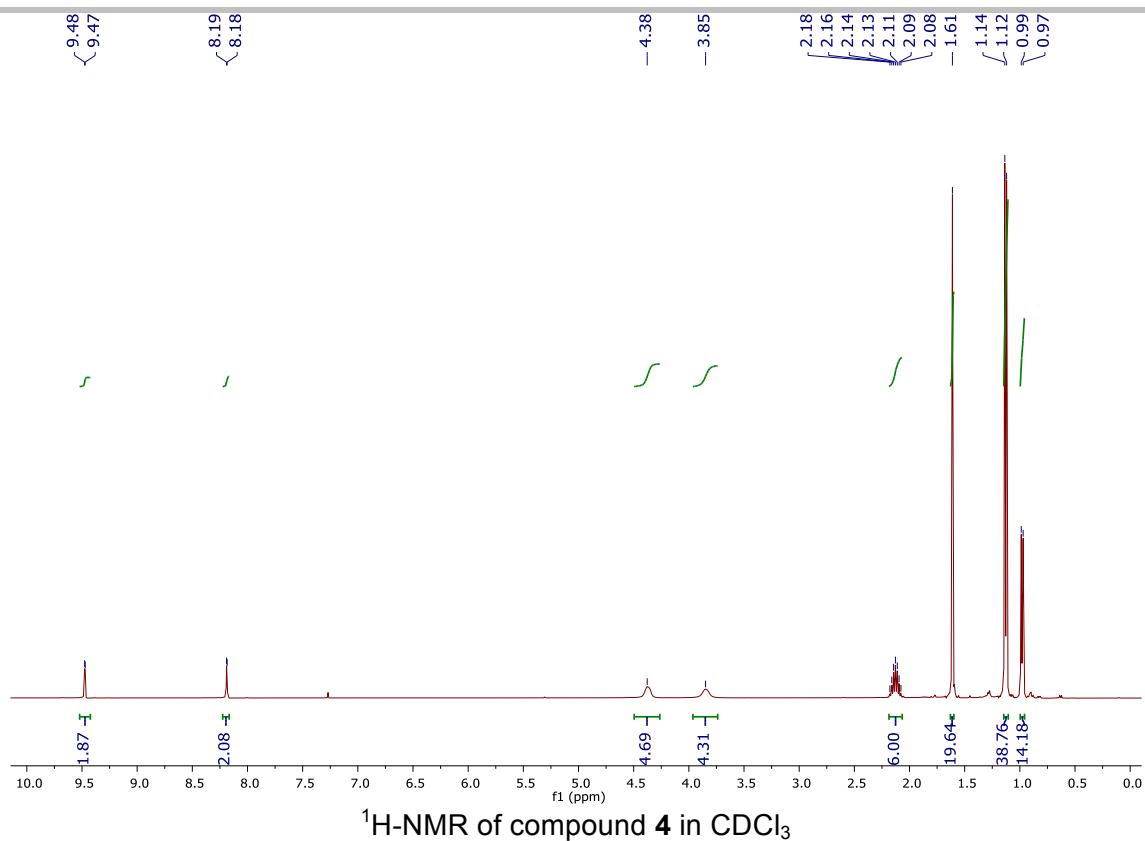
The GFN-xTB Hamiltonian allows computing efficiently systems with up to two thousand atoms^[5] and was used to run Molecular Dynamics (MD) on **NR-10** for 30 ps. This procedure yielded 20 different conformers that were minimized and checked by frequency calculations. Additional **NR-10** conformers were generated by MD with a similar Hamiltonian, and by distorting manually the overall structure of **NR-10**. Selected conformers were minimized with DFT at the B3LYP-6-31g(d,p) level. The **NR-10** conformer with the lowest energy was obtained by MD minimization at the GFN-xTB level, so we applied the same methodology to generate the **NR-20** and **NR-30** conformers, which were subsequently minimized at the DFT level. Note that **NR-20** and **NR-30** are computationally demanding for DFT (with 638 and 918 atoms, respectively). Due to the large size of the high NR, a set of structures, in which the *iso*-butylsilyl groups had been exchanged for a H atom (Figure S3), were also computed in order to quantify the effect of the basis set, namely **NR-10-H**, **NR-20-H**, and **NR-30-H** (with 130, 206 and 282 atoms, respectively, Table S1).

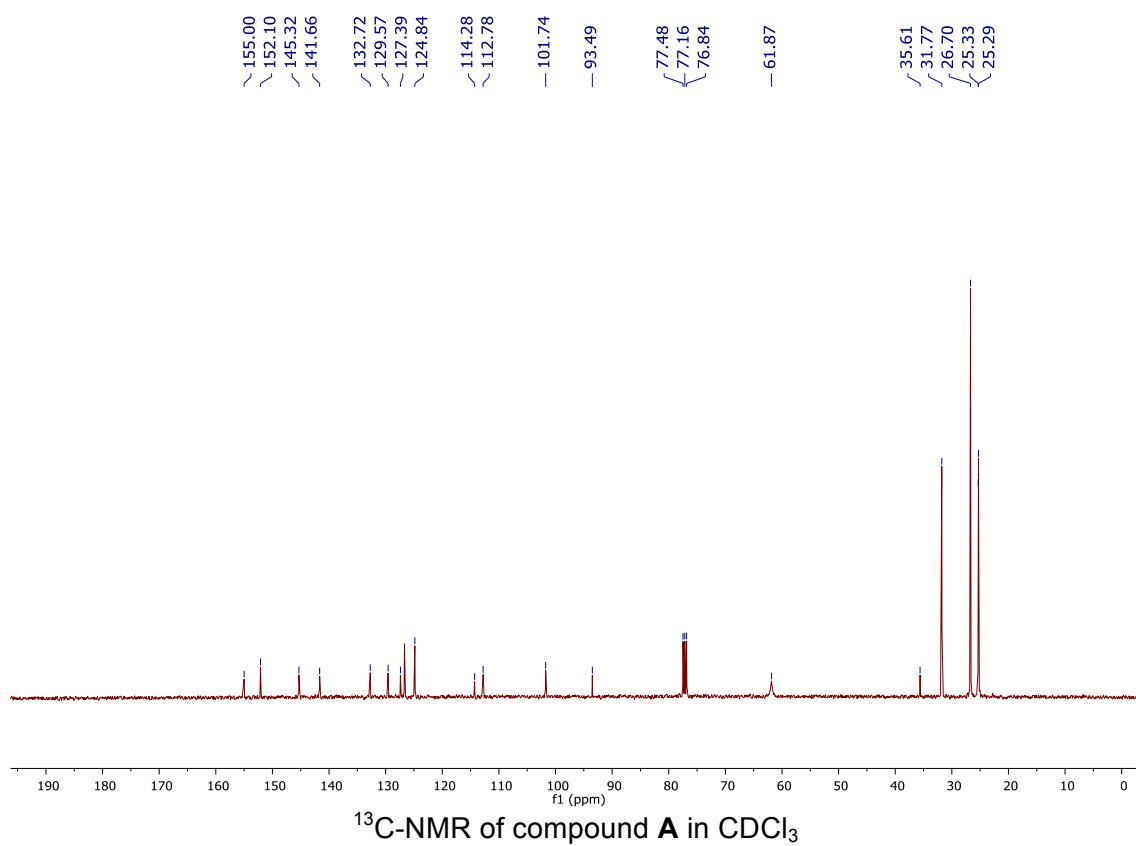
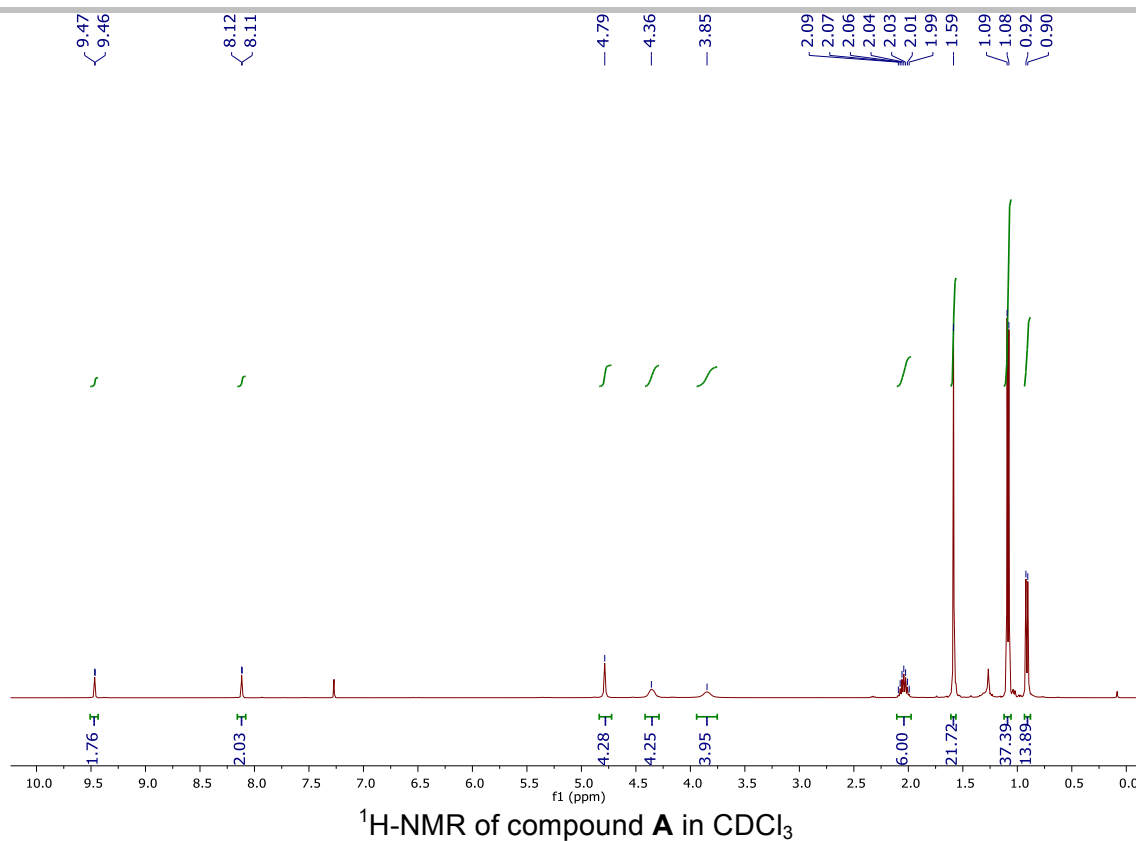
Time-resolved microwave conductivity (TRMC)

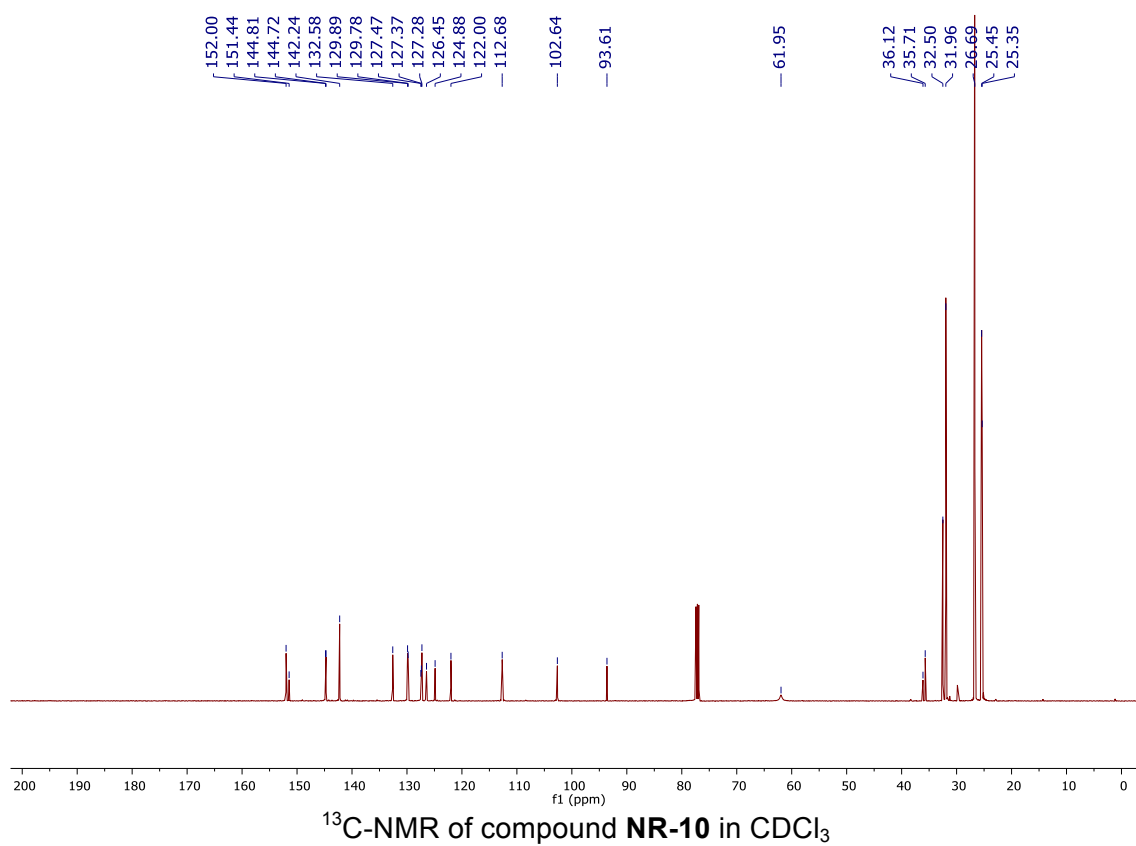
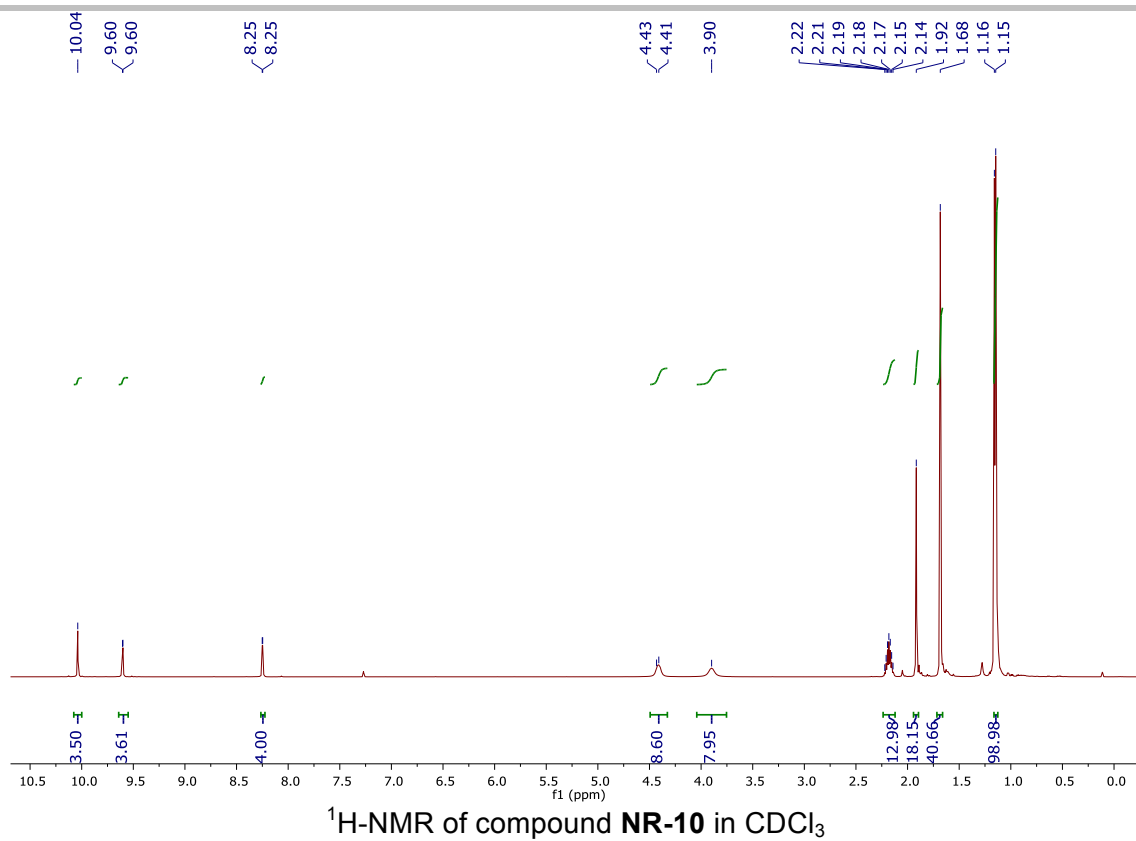
A film on a quartz substrate was set in a resonant cavity and probed by continuous microwaves at ~9.1 GHz. The third harmonic generation (THG; 355 nm) of an Nd:YAG laser (Continuum Inc., Surelite II, 5-8 ns pulse duration, 10 Hz) was used as an excitation source (incident photon density, $I_0 = 9.1 \times 10^{15}$ photons cm^{-2} pulse $^{-1}$). The photoconductivity transient $\Delta\sigma$ was converted to the product of the quantum yield (φ) and the sum of the charge carrier mobilities, $\Sigma\mu (= \mu_h + \mu_e)$ by $\varphi\Sigma\mu = \Delta\sigma(eI_0F_{\text{light}})^{-1}$, where e and F_{light} are the unit charge of a single electron and the correction (or filling) factor, respectively.

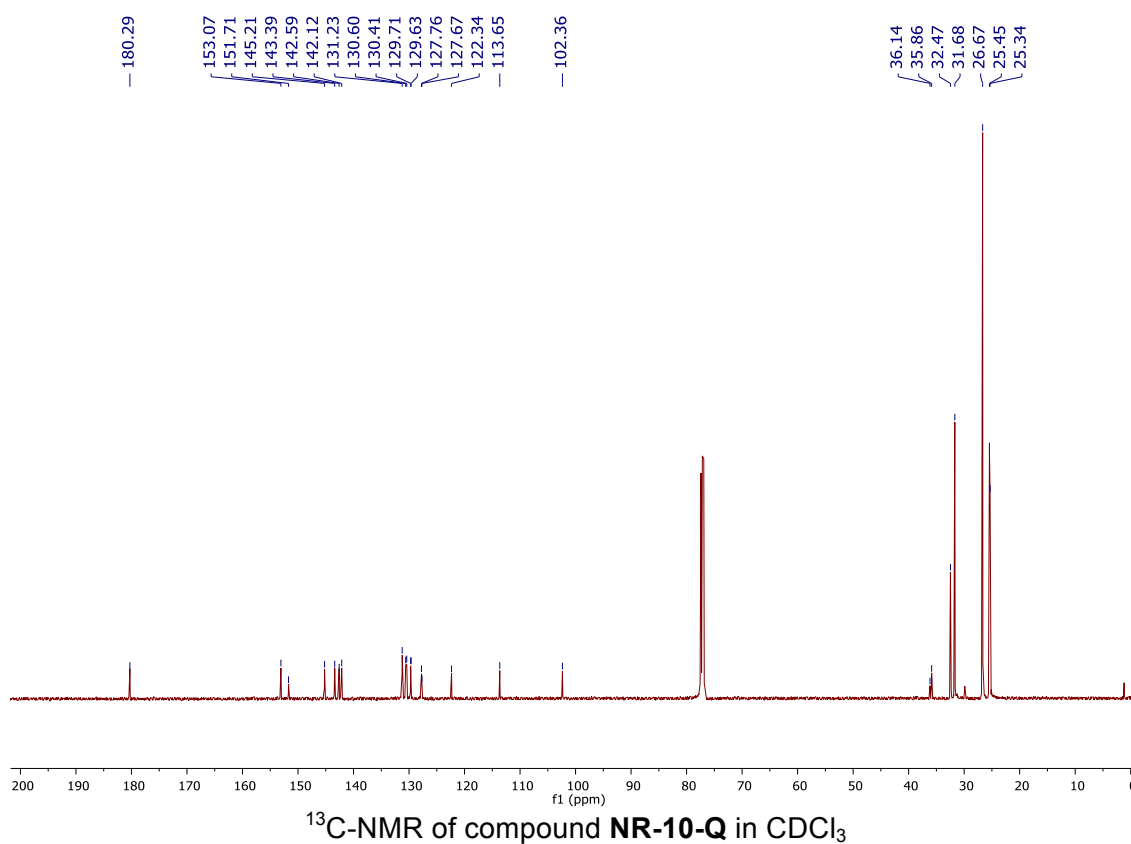
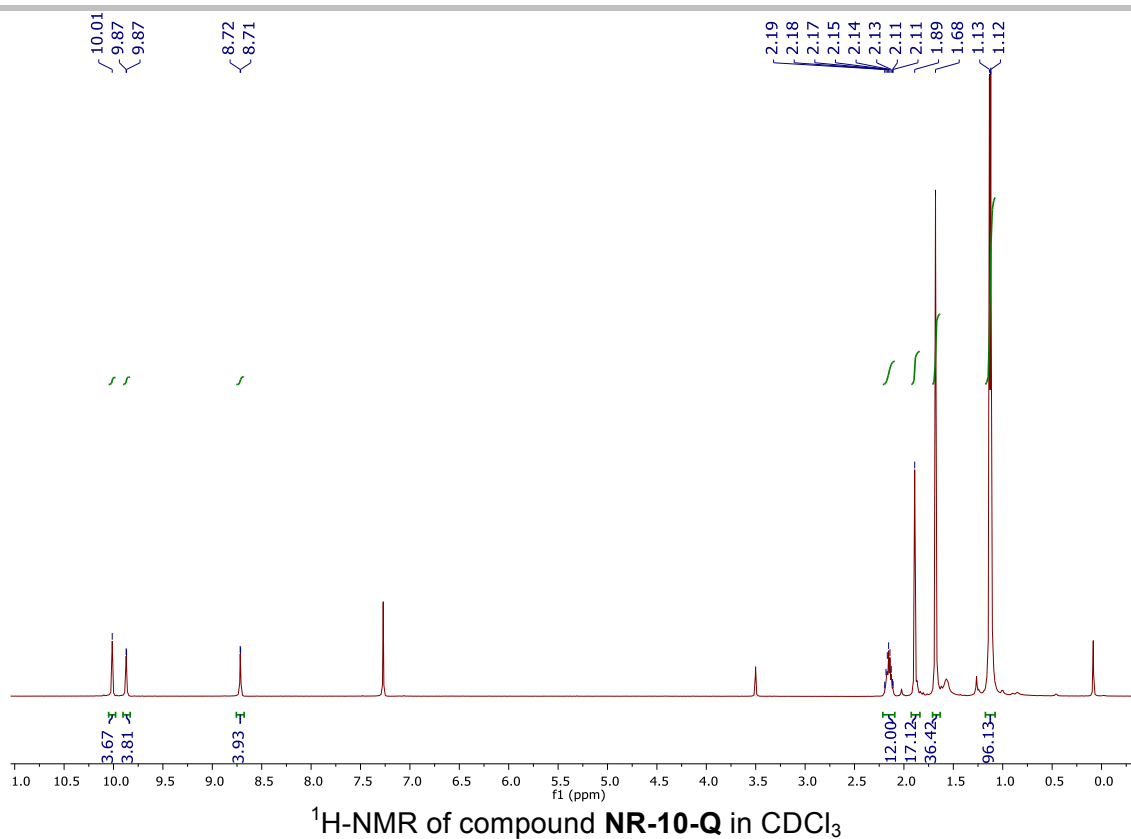
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ SPECTRA

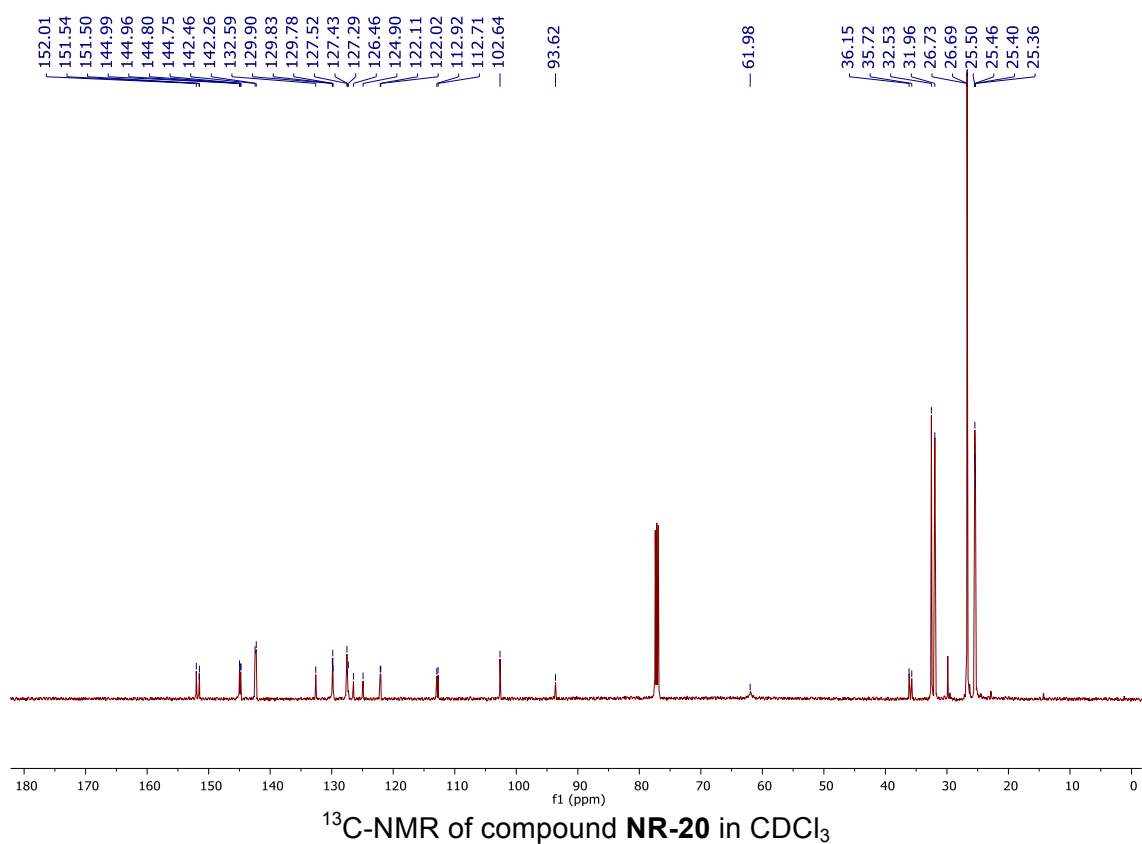
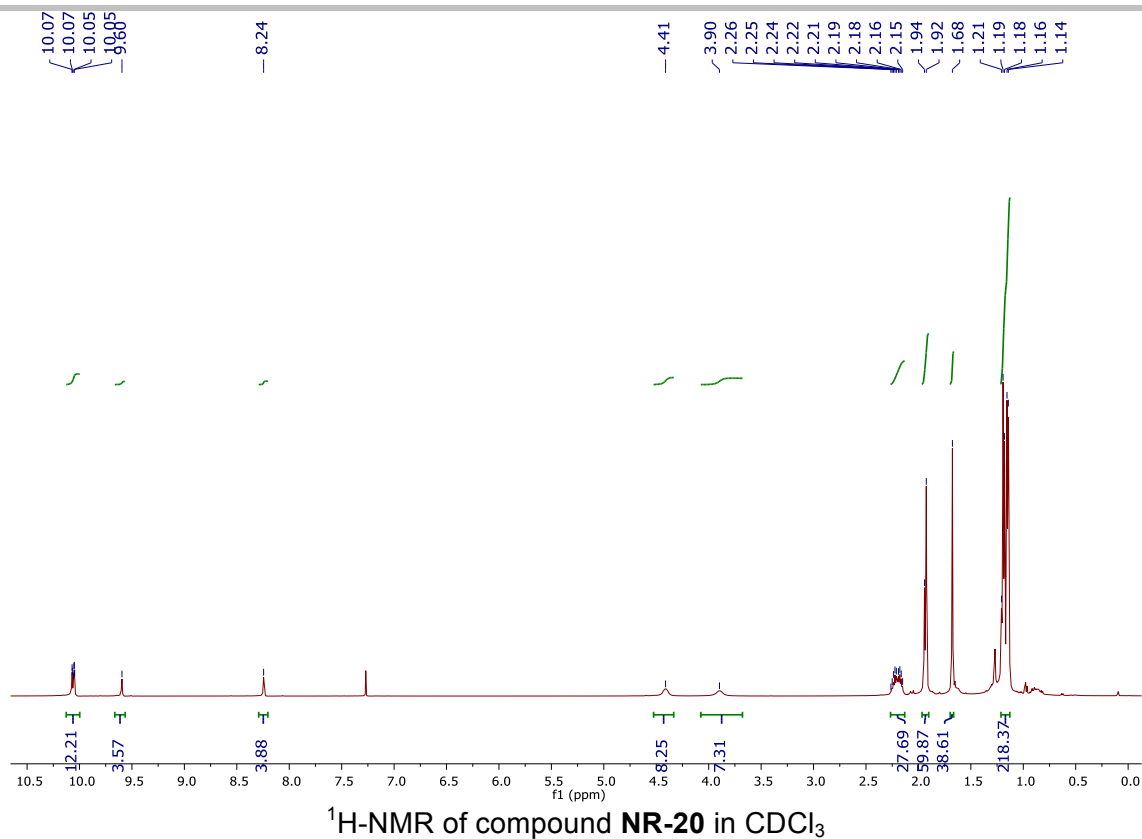


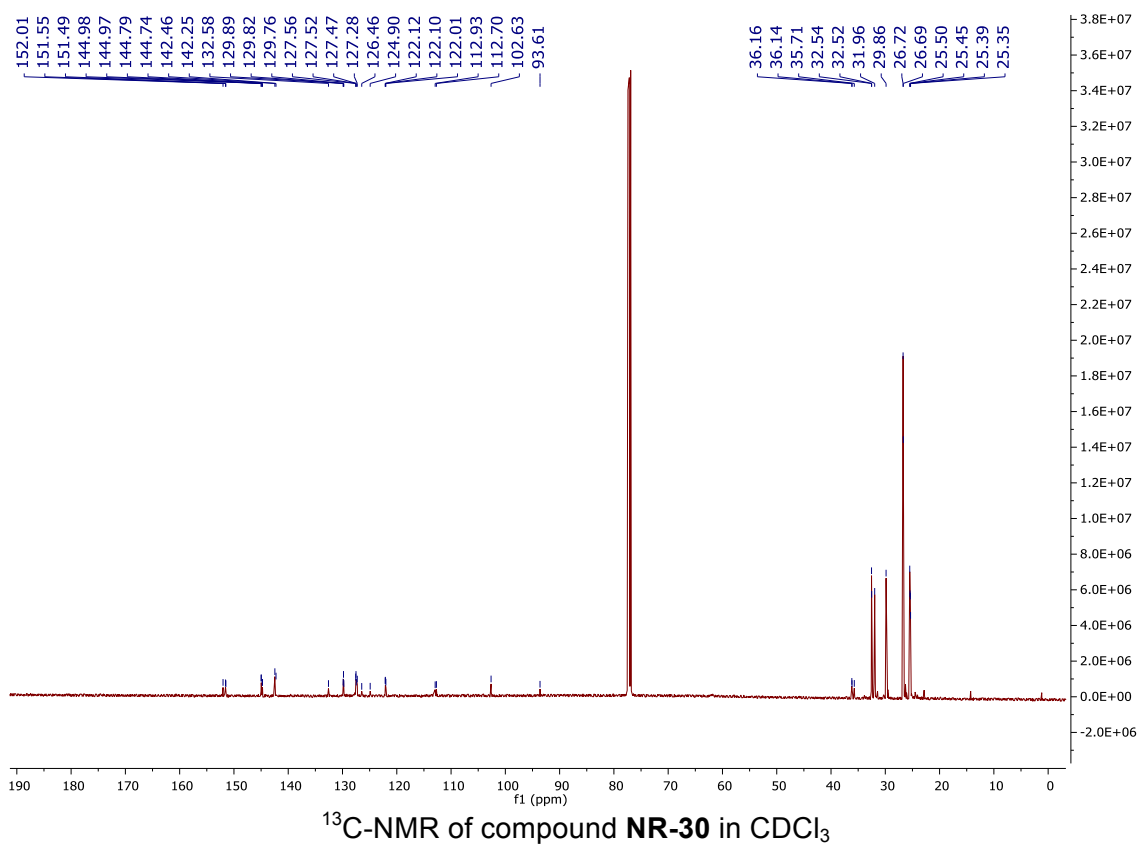
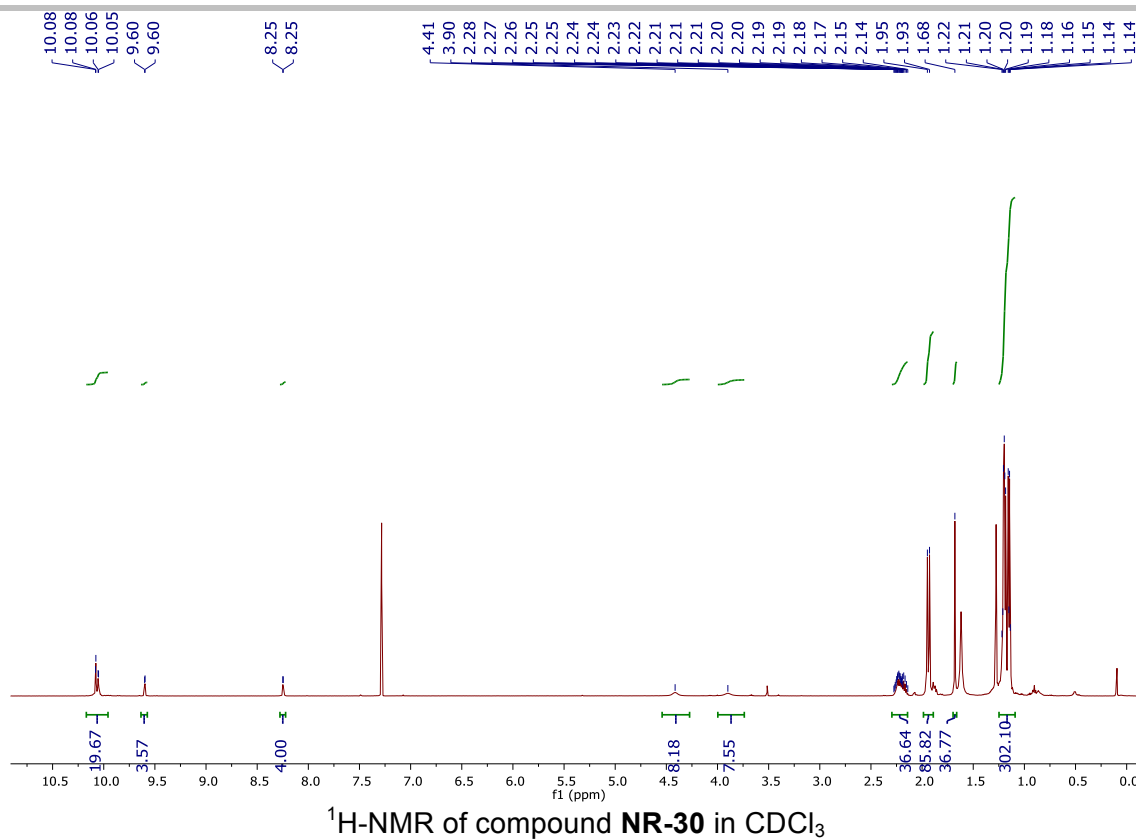












References

- [1] D. Lehnerr, A. H. Murray, R. McDonald, R. R. Tykwinski, *Angew. Chem. Int. Ed.* **2010**, *49*, 6190-6194.
- [2] E. Wang, L. Hou, Z. Wang, S. Hellström, W. Mammo, F. Zhang, O. Inganäs, M. R. Andersson, *Org. Lett.* **2010**, *12*, 4470-4473.
- [3] a) R. García, S. More, M. Melle-Franco, A. Mateo-Alonso, *Org. Lett.* **2014**, *16*, 6096-6099; b) R. Garcia, M. Melle-Franco, A. Mateo-Alonso, *Chem. Commun.* **2015**, *51*, 8037-8040.
- [4] J. Hu, D. Zhang, F. W. Harris, *J. Org. Chem.* **2004**, *70*, 707-708.
- [5] S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **2017**, *13*, 1989-2009.

Author Contributions

D.C.-L. developed the synthetic routes, and carried out the synthesis and characterization of the NRs; J.P.M.-F. synthesised the precursors in large scale; A.S. carried out the TRMC measurements and interpreted the data; K.S. and M.M.-F. carried out the calculations and correlated the results with the experimental optoelectronic data; A.M.-A. conceived and supervised the study and wrote the paper with the input from all authors.