

Porphyrin-LEGO[®]: Synthesis of a Hexafullereno-diporphyrinoid using Porphyrins Programmed for [4+2]-Cycloaddition

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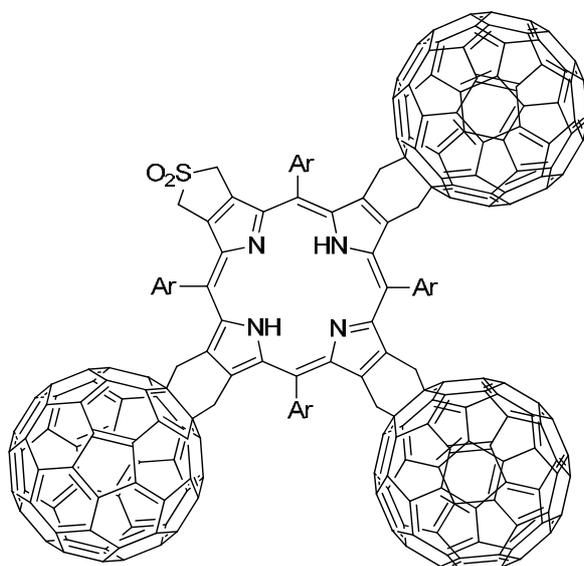
Electronic Supporting Information

General: Materials. 1,2-dichlorobenzene (1,2-DCB), N,N-dimethyl formamide (DMF), carbon disulfide (CS₂), and hexane were from Fluka; dichloromethane, petrol ether (40-60), methanol, toluene were from Acros and were distilled before use. 3-Nitrobenzyl alcohol matrix (NOBA), reagent grade chemical from Fluka, and C₆₀-Fullerene (99.5%) from MER Corp, were used as received. β,β'-Tetrasulfoleno-porphyrin **1**¹ and quinono-porphyrin **4**^{2,3} were synthesized as described. Glassware for all reactions was oven dried at 110 °C and cooled under nitrogen flow prior to use. Reactions, work-up and chromatography were performed under protection from light (alumina foil). Fluka silica gel 60 (230-400mesh). Preparative thin layer chromatography (TLC): Merck 0.25mm silica gel 60 plates. Size

Exclusion Chromatography (SEC): Biobeads SX1 from Bio-Rad Corp, High vacuum (HV): *ca.* 0.05 mbar.

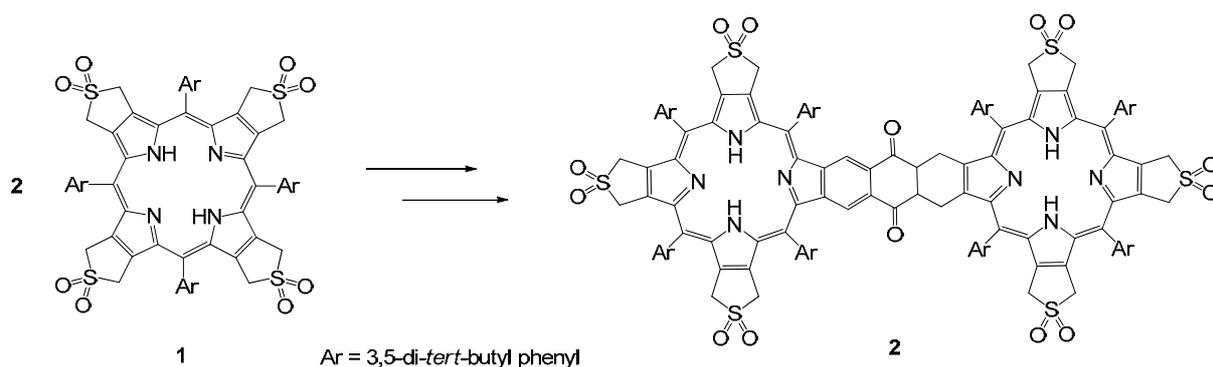
Spectroscopy. UV/Vis spectra: *U 3000 spectrometer (Hitachi)*, in 1mm or 10mm quartz cells, λ_{\max} (log ϵ) in nm. Fluorescence spectra: *Varian Cary Eclipse*, excitation (λ_{exc}) and emission wavelengths (λ_{em} (intensity)) λ in nm. Nuclear magnetic resonance (^1H - and ^{13}C -NMR) spectra: *Varian 500 MHz* at 298K; chemical shifts (δ) in ppm, with $\delta(\text{CHCl}_3)=7.26$ ppm, $\delta(^{13}\text{CHCl}_3)=77.2$ ppm; $\delta(\text{CHDCl}_2)=5.32$ ppm, $\delta(^{13}\text{CH}_2\text{Cl}_2)=53.8$ ppm; FAB-MS: *Finnigan MAT-95*, positive ion mode, 3-nitrobenzyl alcohol (NOBA) matrix; m/z (rel. intensity %); MALDI-TOF-MS: *Bruker Ultraflex MALDI-TOF*, positive ion mode, matrix: 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB), m/z (rel. intensity %).

Structure modelling. Structural models were calculated using the OPLS-AA force field⁴ as implemented in the MOE 2011.10 modelling package. Starting from a crystal structure of the trisfullerenoporphyrin **7**⁵ several distinct starting structures of **Ni₂-6** were generated. To build the dimer **Ni₂-6**, the structure of the non-planar **7** was duplicated (in two different relative orientations) and the remaining SO₂ unit of **7** was replaced by the quinone linker using MOE 2011.10. Ni²⁺-ions were inserted at the center of each of the porphyrins. Subsequently covalent bonds were defined from each Ni²⁺-ion to the corresponding porphyrin nitrogens. Several unique starting points were constructed by slightly changing the fullerene positions. Planar geometry was specified as a parameter for the direct Ni²⁺-coordination. Thereafter the systems were minimized using the OPLS-AA force field. Minimization was performed in a distance dependent dielectric with a relative permittivity of 4.8 corresponding to the permittivity of CHCl₃. Two distinct minimum structures (of C₂- and C_{2h}-symmetry) were obtained.



Formula of the trisfullereno-porphyrin **7**
(Ar = 3,5-di-*tert*-butyl-phenyl)

S1. Synthesis of metal-free dimeric porphyrin 2

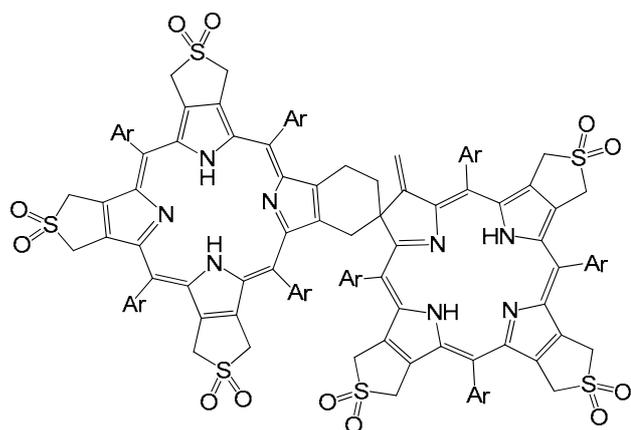


Two 10 mL round-bottomed flasks were each charged with 10 mg sulfonated-porphyrin **1** (7.02 μmol) and 1.5 g of silica gel 60 (w/w 1:150). 5 mL of CH_2Cl_2 was added to both flasks, the suspension was sonicated for 5 min and the solvents were evaporated on rotary evaporator. This procedure was repeated twice and the resulting mixture was dried on HV for 1h with argon purging to obtain a pink coloured powder loaded with **1**. The flasks were placed under argon (from filled balloons) and immersed in a pre-heated oil bath at 140°C. The reaction mixture was heated for 45 min and then the flasks were removed from the oil bath to cool down to room temperature under argon. Brownish yellow silica gel powders loaded with thermolysis products derived from **1** were obtained.

Another dry 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with 30 mg (20.5 μmol) of quinono-porphyrin **4** and 8 mL of abs CH_2Cl_2 . To the brown solution, 1 mL of $\text{BF}_3 \cdot \text{OEt}_2$ (48% solution, 3.98 mmol, 194 equiv. with respect to **4**) was added under argon, and the solution turned to dark green. To this dark green solution at room temperature, small portions (50 - 100 mg) of the brown silica gel powder (loaded with the thermolysis product from **1**) were added every 5-10 min. The additions were completed within 3 hours and the slurry was stirred for additional 30 min. The reaction mixture was diluted with CH_2Cl_2 (40 mL), filtered through a Buchner funnel, and the solution was washed with sat. aq. NaHCO_3 (2 x 50 mL). The aqueous phase was extracted with CH_2Cl_2 (4 x 40 mL) until the organic extracts turned colourless. The combined organic phases were washed with aq. NaHCO_3 (50 mL), filtered through a plug of dry cotton. The solvents were removed under reduced pressure and the crude brown material obtained was purified by size exclusion column chromatography. For this purpose, the crude mixture was dissolved in 6 mL of toluene-THF(1:1, v/v), loaded on the SEC column (Biobeads SX1, 45 x 3.5 cm) and eluted with toluene-THF (1:1, v/v) under gravity flow. First a diffused brown band eluted that exhibited characteristic chlorin type absorptions at 680 nm, followed by the high molecular

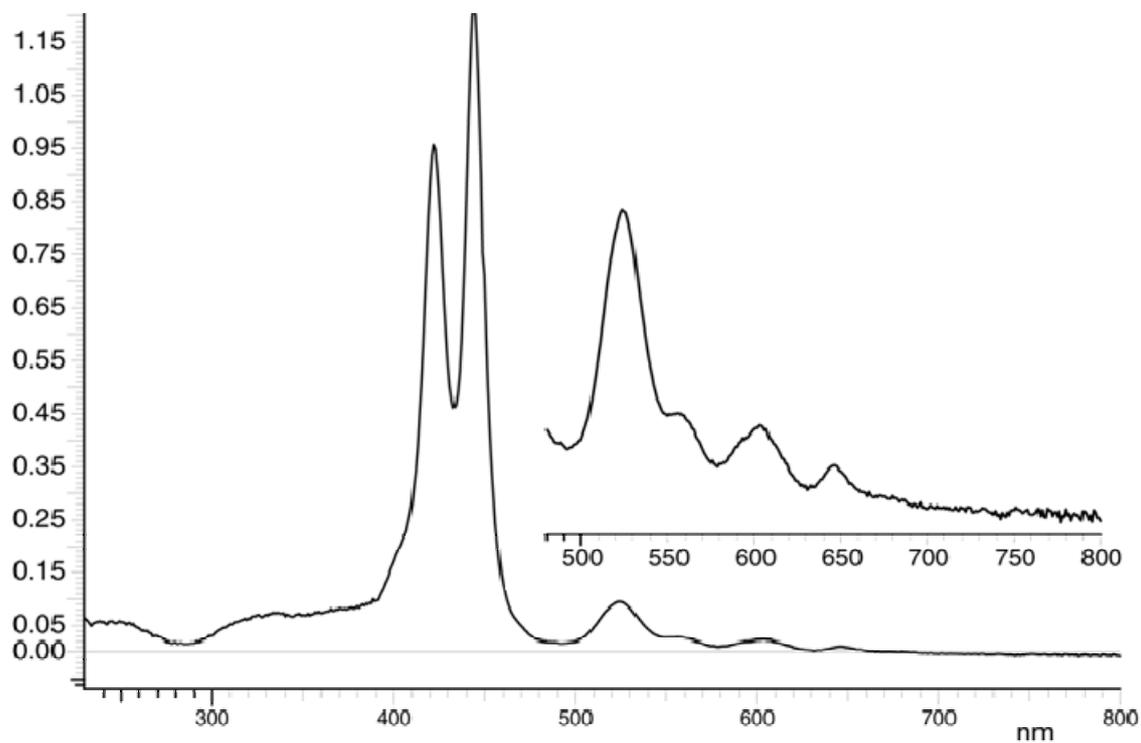
weight fraction (SEC-fraction1), and later the low molecular weight mixture, SEC- fraction2, which contained both un-reacted starting porphyrins (**1** and **4**). Solvents were removed from the SEC-fraction1 under reduced pressure. The residue was purified on preparative TLC plates (1:5 of toluene/CH₂Cl₂, v/v). Two major bands separated, of the apolar spirodimeric by-product **8** (SEC F1-1) and the dimer **2** (SEC F1-2). They were scratched from the plates. The samples of silica gel with adsorbed products were loaded onto a 4-5 cm silica gel columns and eluted with 1-2% of MeOH in CH₂Cl₂. Each of the two eluted solutions (with one of the two products, **2** and **8**) was dried under reduced pressure. The residue was re-dissolved in CH₂Cl₂ for transfer into small vials. The two dimers (**2** and **8**) were each precipitated with excess of MeOH and the resulting precipitates were dried overnight on HV at 50°C, giving 3.2 mg (8.1%; 16.4% based on recovered **1**) of quinone bridged dimeric porphyrin **2** (analyzed as described below) and 2.9 mg (7.5%; 15.2% based on recovered **1**) of spiro dimeric porphyrin **8** (which was identified tentatively by its UV/Vis-spectrum)^{3,6}.

Metal-free dimeric porphyrin **2**: *UV/Vis* (CH₂Cl₂, c = 2.21 x 10⁻⁵ M, see Figure S1A): 646 (3.70), 603 (4.04), 559 (4.10), 524 (4.63), 444 (5.74), 422 (5.64), 402 sh (4.93), 326 (4.51), 248 (4.43); *Fluorescence* (CH₂Cl₂, c = 7.08 x 10⁻⁶ M, λ_{EX} = 525 nm (O.D = 0.35)): λ_{EM}(a.u.): 680 (52), 739 (64) (see Figure S1B). *¹H-NMR* (300 MHz, in CDCl₃, 25 °C): -3.25, -2.94, -2.71 (3 br s, 4NH), 1.32, 1.39, 1.46 (3s), 1.50-1.52 (overlapping signals, in total 144H, 16 tert-butyl groups), 2.76 (br dd, *J* ~ 17 & 5 Hz, 2H), 3.31 (br dd, *J* ~ 17 & 5Hz, 2H), 3.54 (br t, *J* ~ 5Hz, 2H), 3.93-4.37 (m, 24H), 7.63 -7.66 (m, 4H), 7.79 – 7.84 (m, 13H), 7.93 - 8.01 (m, 8H). *FAB-MS* (C₁₇₄H₂₀₄N₈O₁₄S₆: (*m/z*)_{calc.} = 2821.381): *m/z* (%): 2827.2 (10), 2826.5 (14), 2825.6 (39), 2824.5 (48), 2823.5 (42), 2822.5 (24, [M+H]⁺), 2821.5 (11, M⁺), 2760.6 (14), 2759.6 (20), 2758.7 (8, [M – SO₂+H]⁺), 2757.3 (7), 2756.3 (9), 2441.6 (32), 2440.5 (24), 2439.6 (27), 2438.7 (32, [M – 6 SO₂+H]⁺), 2437.9 (78), 2436.7 (100), 2435.8 (56), 2434.9 (61), 2433.7 (41), 2428.7 (35).



Formula of spirodimer **8**
 (Ar = 3,5-di *tert*-butyl phenyl)

A



B

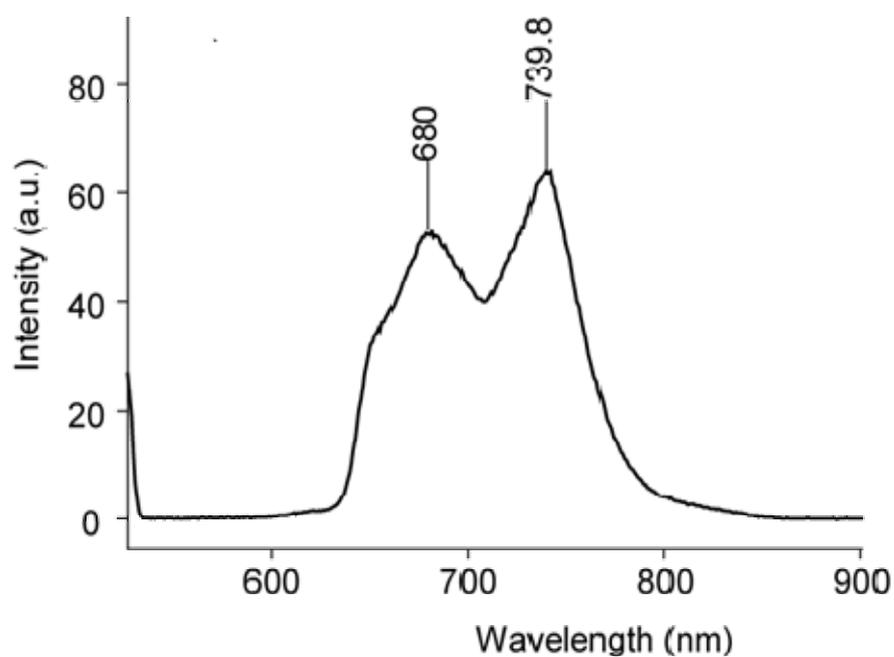
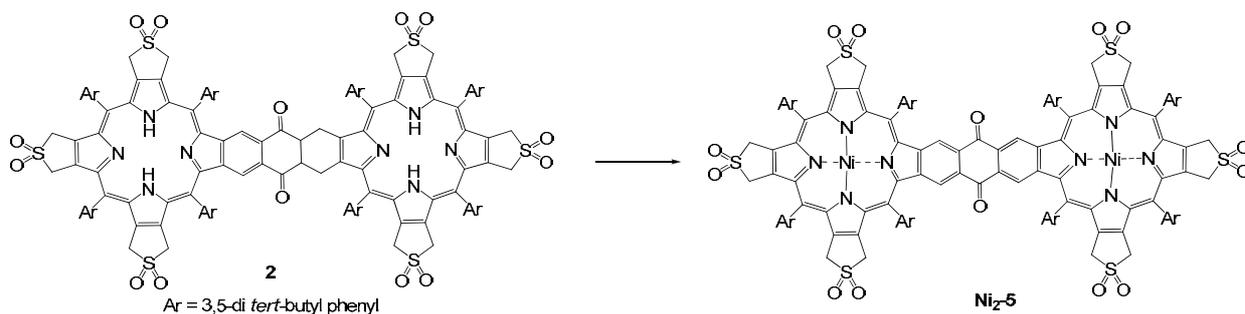


Figure S1. UV/Vis-spectrum (**A**) and fluorescence emission spectrum (λ_{Ex} at 525 nm, **B**) of 2,3-dihydroquinone-bridged porphyrin dimer **2** (in CH_2Cl_2 , $c = 2.21 \times 10^{-5}$ M, 1 mm path length).

S2. Synthesis of Ni-porphyrin dimer Ni₂-5.



A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 1.7 mg (0.603 μmol) of hexafulfeno-diporphyrin **2**, DMF (5 mL), 15 mg of $\text{Ni}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (70.5 μmol , 120 equiv.). The resulting brown suspension was stirred in an oil bath at 85°C for 5 h under open air. The reaction progress was monitored by UV/Vis spectroscopy for the metal insertion as observed by the loss of characteristic Q bands. After completion of the reaction, the cold reaction mixture was washed with sat. aq. NaHCO_3 (2 x 25 mL), and the aqueous phase was extracted in toluene (5 x 15mL) until the organic extracts had no colour. The combined organic phases were washed again with aq. NaHCO_3 (pH ~9, 2 x 30 mL) and filtered through a plug of dried cotton. All solvents were evaporated under reduced pressure and the sample was dried under HV. The dry residue was applied in CH_2Cl_2 on a preparative TLC plate, which was developed with toluene- CH_2Cl_2 (1:6, v/v).

The major brown band that ran on top was scratched from the plate and the silica gel powder with adsorbed product was applied to a 4-5 cm silica gel 60 column. The brown compound eluted with CH_2Cl_2 which was then removed under reduced pressure. The residue was re-dissolved in CH_2Cl_2 (1 mL), the solution was transferred into a small vial and raw dimer was precipitated with MeOH (4 mL). The obtained black precipitate was dried under HV at 50°C for 15 h to give 1.4 mg (78%) oxidized quinone bridged dimeric porphyrin **Ni₂-5**.

TLC: toluene- CH_2Cl_2 ; 1:6; R_f = 0.5. *UV/Vis*: (CH_2Cl_2 , $c = 4.78 \times 10^{-6}$ M, see main text, Figure 1): 597 (4.59), 559.5 (4.43), 482 (4.87), 450.5 (5.05), 425 (4.96), 339.5 sh (4.44), 314.5 (4.52). *Fluorescence* (CH_2Cl_2 , $c = 4.78 \times 10^{-6}$ M, $\lambda_{\text{Ex}} = 559$): no emission observed. *¹H NMR* (300MHz, in CDCl_3 , 300K, see Tabler S1): 1.47, 1.49 (2 s, 144H), 4.06 (br s, 24H), 7.66 (d, $J = 1.5\text{Hz}$, 8H), 7.75 (d, $J = 1.5\text{Hz}$, 8H), 7.86 (t, $J = 1.5\text{Hz}$, 4H), 8.04 (t, $J = 1.5\text{Hz}$, 4H), 8.08 (s, 4H). *FAB-MS* ($\text{C}_{174}\text{H}_{196}\text{N}_8\text{O}_{14}\text{S}_6\text{Ni}_2$: $(m/z)_{\text{calc.}} = 2929.189$): m/z (%): 2939(5), 2938.1(21), 2937.2(16), 2936.3(19), 2935.3(26), 2934.3(29), 2933.4(28), 2932.6(30), 2931.9(19),

2931.1(22), 2930.2(17, [M+H]⁺), 2929.4(13), 2928.6(12), 2927.6(11), 2557(48), 2555.9(40), 2553.8(42), 2552.9(36), 2551.9(37), 25501(46), 2550.0(59), 2549.0(69), 2548.3(39), 2547.8(59), 2546.9(80, [M-6SO₂+H]⁺), 2545.9(100, [M-6SO₂]⁺), 2544.9 (85), 2543.9(79), 2542.9(73), 2541.8(56), 2540.8(45), 2536.8(37), 2535.8(44), 2534.7(50).

Table S1: ¹H-NMR- and ¹³C-NMR-signal assignment for **Ni₂-5** (300 MHz, CDCl₃) with correlations from ¹H,¹³C-HSQC-, ¹H,¹³C-HMBC- and ¹H,¹H-COSY-spectra.

Atom No	δ ¹ H	δ ¹³ C	Atom No	δ ¹ H	δ ¹³ C
1			7		137.8§
2		142.9§	71	4.06	56.7
21	8.08	124.6	9		
22		130	10		120.3
23		180.4	101		
5		118.1	102	7.66	126.4
51			103		152.1
52	7.75	126.8	1031		35.3
53		152.1	1032	1.49	31.8
531		35.3	104	7.86	123.6
532	1.47	31.8	11		
54	8.04	123.6	12		136.2§
6			121	4.06	56.7

§: tentatively assigned signal.

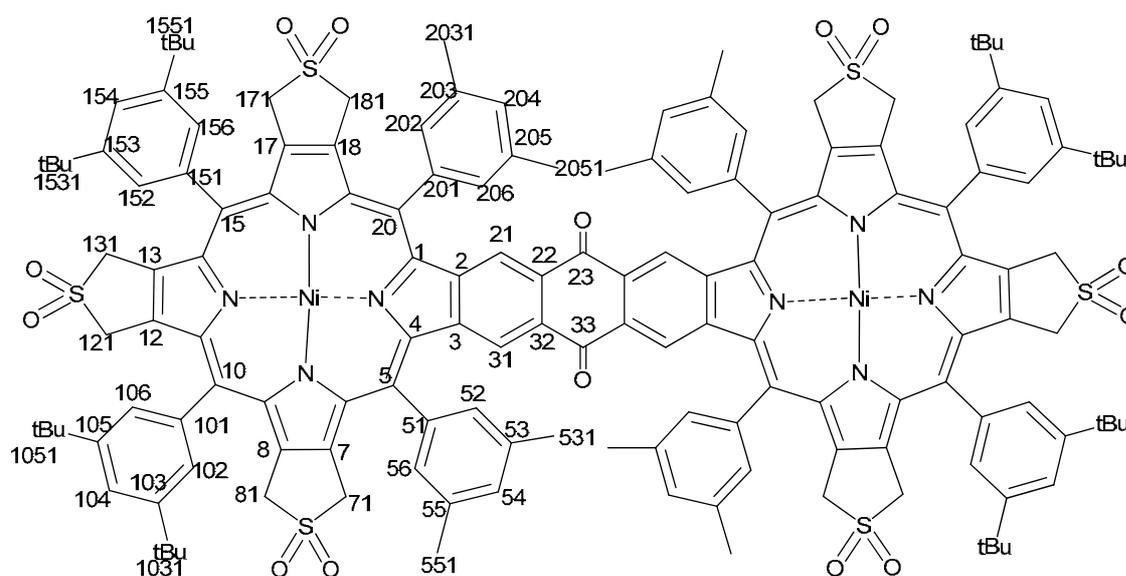
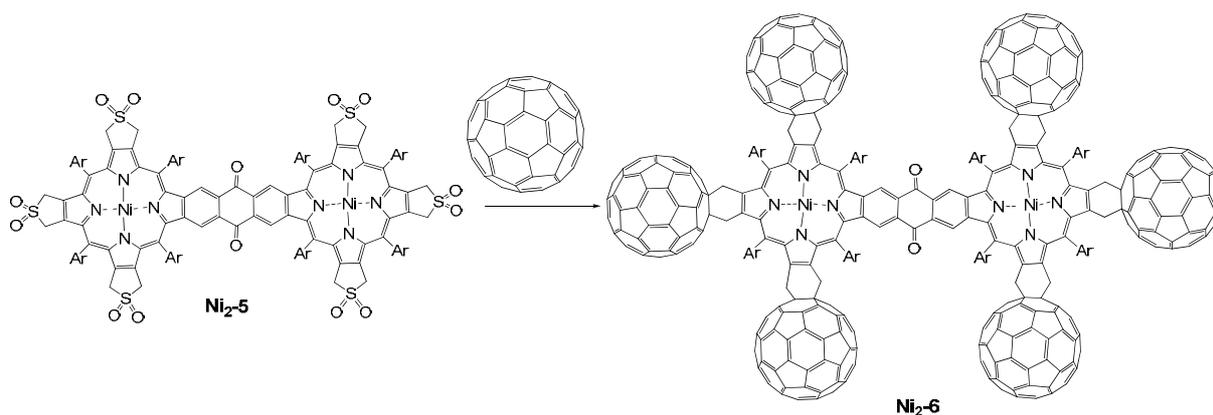


Figure S2. Atom numbering used here for **Ni₂-5**

S3. Synthesis of hexafullereno-di-Ni-diporphyrin Ni₂-6.



A dry, argon flushed 50 mL two-necked round-bottom flask equipped with a magnetic stir bar was charged with 2.2 mg dimeric nickel porphyrin **Ni₂-5** (0.75 μmol), 45 mg of C₆₀-fullerene (62.5 μmol , 83 equiv.) and 7 mL of 1,2-dichlorobenzene (1,2-DCB). The resulting red solution was flushed with argon and degassed by freeze and thaw technique (freezing in liquid N₂ while applying HV and releasing under argon). This procedure was repeated twice and the mixture was placed under an argon filled balloon. The resulting brown solution was immersed in a pre-heated oil bath at 140°C and stirred under argon. The reaction progress was monitored with HPLC by taking an aliquot of 30 μL . After 23h of stirring, the flask was removed from the oil bath and the reaction mixture was allowed to cool down under argon. The cold reaction mixture was loaded on the SEC column (2 x 25 cm) in 1,2-DCB and eluted with toluene under gravity flow. This eluted first a fraction (SF1) of the high molecular weight product **Ni₂-6**, followed by un-reacted C₆₀ (SF2). All solvents were removed under reduced pressure, and the product fraction (SF1) was re-purified on a silica gel 60 column (10 x 2 cm). The SF1 fraction was loaded on the column in 1:1 CS₂/hexane mixture. Elution with 2:1 of CS₂/hexane mixture (v/v) gave the green fraction (SF1-F1) of the hexa-fullerene addition product **Ni₂-6**. Solvents were again removed under reduced pressure and the residue was re-dissolved in CS₂ and transferred into a small vial. The Ni-complex **Ni₂-6** was precipitated with CH₂Cl₂/MeOH. The precipitate was washed with diethyl ether and dried on HV at 50°C for 15 h to give 4.1 mg (79.5%) of hexafullerene adduct **Ni₂-6**.

UV/Vis: (toluene, $c = 1.51 \times 10^{-5}$ M, see main text, Figure 1): 617 (4.76), 569.5 (4.53), 500.5 (4.89), 465 (5.03), 433.5 (5.14), 325.5 (5.34). *¹H NMR* (500 MHz, in 1:1 CD₂Cl₂/CS₂, at 25°C, see Figure S3): 1.09, 1.26, 1.44, 1.46, 1.49, 1.81, 1.88 (^tBu), 4.03-4.11 (overlapped d), 4.89-4.97 (overlapped d), 7.82 (s), 7.85-7.87 (overlapped s), 7.92 (s), 8.00 (s), 8.05. 8.06

(overlapping s), 8.17 (s), 8.19 (s), 8.23 (s), 8.39 (s), 8.44 (s). $^1\text{H NMR}$ (500 MHz, in 1:1 $\text{CD}_2\text{Cl}_2/\text{CS}_2$, at 10°C , see Figure S3): 1.07, 1.24, 1.42, 1.45, 1.47, 1.803, 1.87 (^tBu), 3.99, 4.01, 4.02, 4.04, 4.06, 4.09 (overlapped d's), 4.89, 4.92, 4.94, 4.95 (overlapped d's), 7.80 (br s), 7.84 (br s), 7.85 (br s), 7.90 (br s), 7.98 (br s), 8.04 (3 br s), 8.15 (br s), 8.17, 8.18, 8.19 (3 br s), 8.22 (br s), 8.39 (br s), 8.43 (br s). *MALDI-TOF MS*: (DCTB matrix) m/z (%): 6873.5 (0.7, not resolved isotope cluster of quasi-molecular ion $\text{C}_{534}\text{H}_{197}\text{N}_8\text{O}_2\text{Ni}_2^+$, see Figure S4 panel A and S5 panels B and C); 2548.1 (100, isotope cluster of $[\text{C}_{534}\text{H}_{196}\text{N}_8\text{O}_2\text{Ni}_2 - 6 \text{C}_{60}]^+$, see Figure S4 panel A and S5 panel A). Post Source Decay (PSD) *MALDI-TOF-MS* (DCTB matrix; ion deflection up to m/z 6870): 6875.8 (10, $\text{C}_{534}\text{H}_{196}\text{N}_8\text{O}_2\text{Ni}_2^+$), 6239.0 (97, $[\text{C}_{534}\text{H}_{196}\text{N}_8\text{O}_2\text{Ni}_2 - \text{C}_{60}]^+$), 5620.0 (95, $[\text{C}_{534}\text{H}_{196}\text{N}_8\text{O}_2\text{Ni}_2 - 2 \text{C}_{60}]^+$), 5024.0 (100, $[\text{C}_{534}\text{H}_{196}\text{N}_8\text{O}_2\text{Ni}_2 - 3 \text{C}_{60}]^+$), 4533.0 (29, $[\text{C}_{534}\text{H}_{196}\text{N}_8\text{O}_2\text{Ni}_2 - 4 \text{C}_{60}]^+$), see Figure S4 panel B.

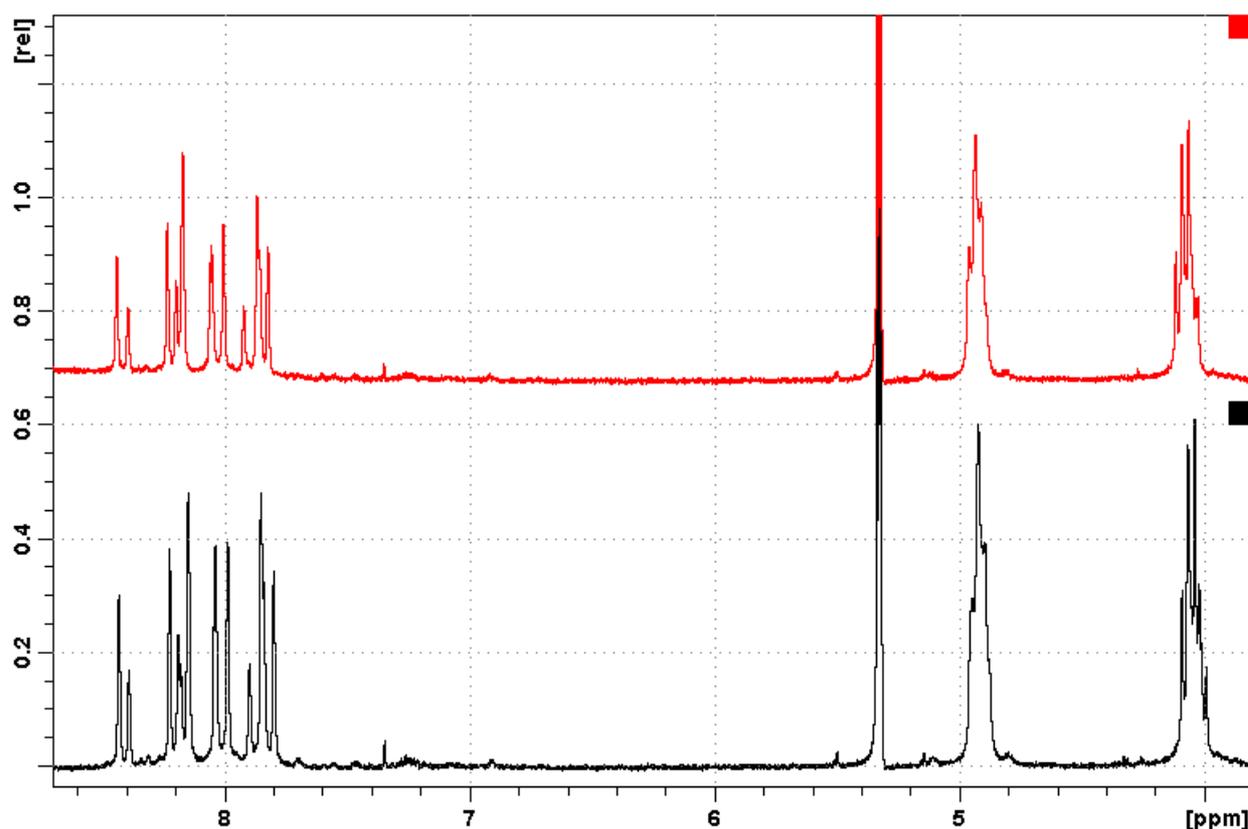


Figure S3. Low field section of the $^1\text{H-NMR}$ -spectra of the hexafullereno-Ni-porphyrin dimer $\text{Ni}_2\text{-6}$ at 25°C in $\text{CS}_2 : \text{CD}_2\text{Cl}_2$ (1 : 1) (top, red trace) and at 10°C (bottom, black trace) with signals of aromatic H-atoms (at > 7 ppm) and of the methylene groups (4 – 5 ppm) that are attached to the fullerene addends.

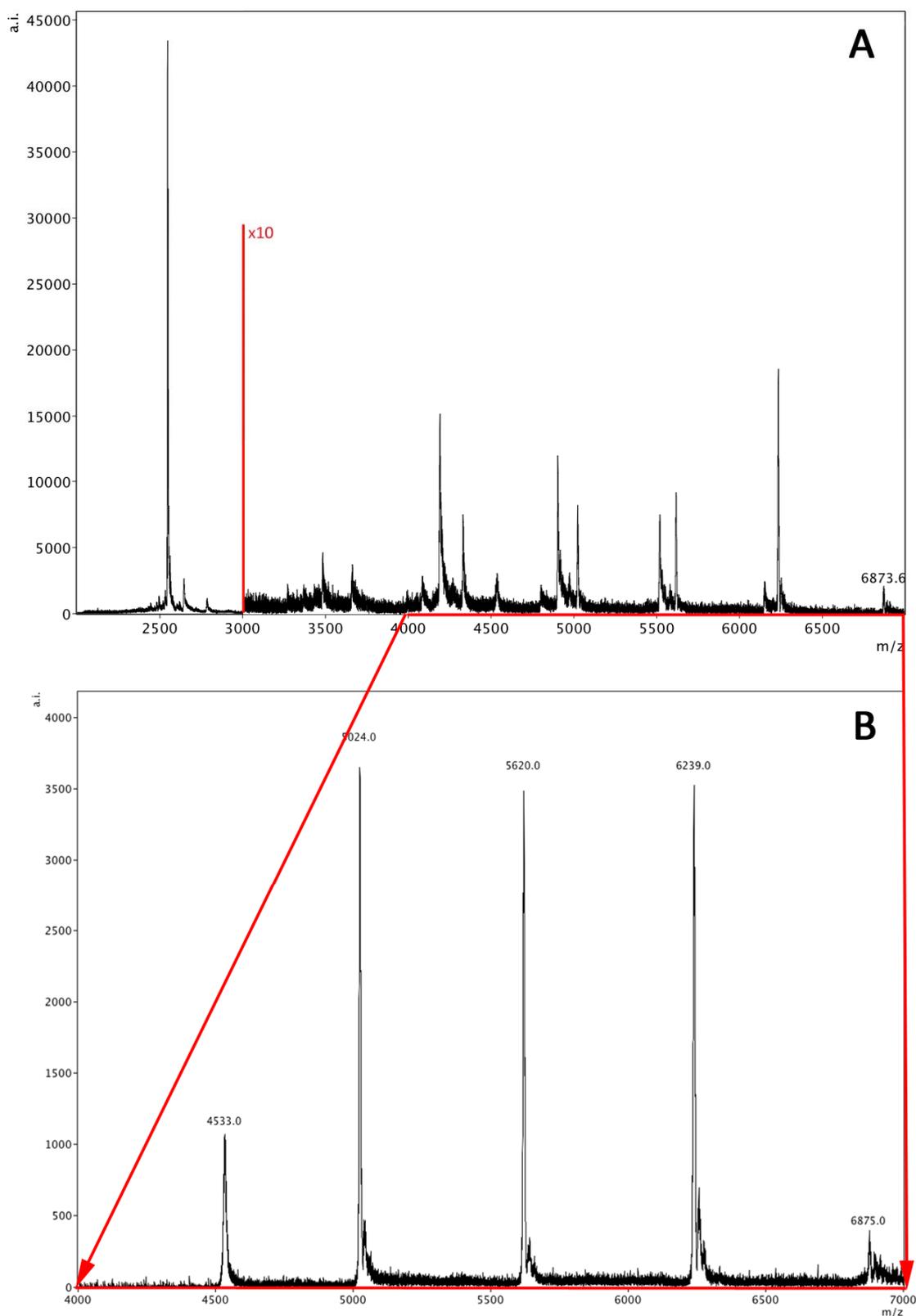


Figure S4. Panel A: MALDI-TOF-MS spectrum of $\text{Ni}_2\text{-6}$ in DCTB matrix. Panel B: Post Source Decay MALDI-TOF-MS (DCTB matrix; ion deflection up to m/z 6870) showing the fragmentation pattern caused by dissociation of meta-stable molecular ions (consecutive loss of C_{60} units is indicated).

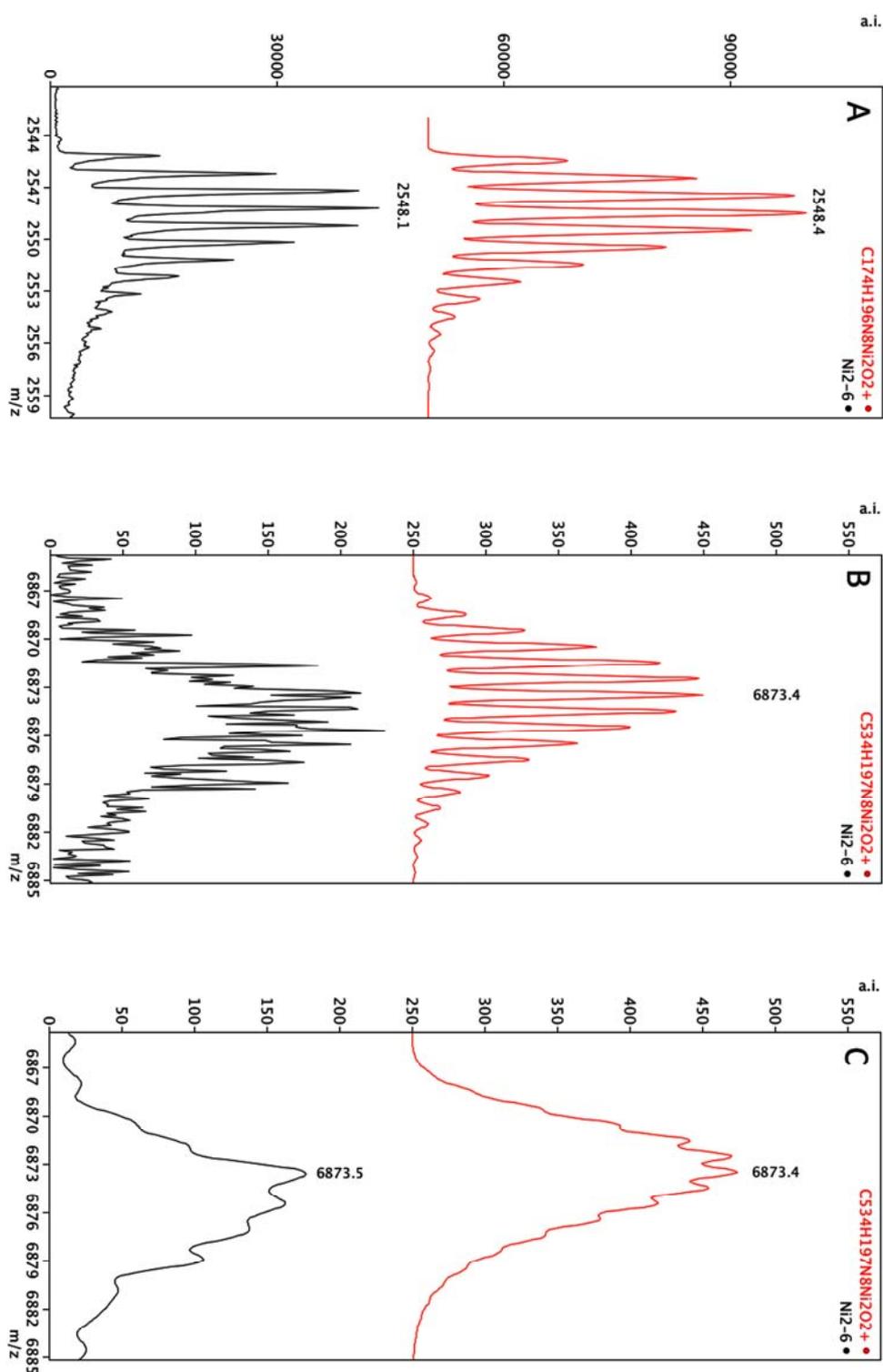


Figure S5. Isotopic clusters of quasi-molecular ion at m/z 6874 and of the major fragment ion at m/z 2548 in the MALDI-TOF-MS spectrum of $\text{Ni}_2\text{-6}$ in DCTB matrix. Simulated spectra are superimposed and highlighted in red. Panel A: Major fragment ion corresponding to the loss of six C_{60} units. Panel B: Quasi-molecular ion; upper (red) trace was simulated with a peak width of 0.5 Da. Panel C: Quasi-molecular ion; upper (red) trace was simulated with a peak width of 1 Da; spectrum smoothed using a Savitzky–Golay filter.

Table S2: ^1H -NMR- and ^{13}C -NMR-signal assignment for **Ni₂-6**, major conformer (500 MHz, 1:1 $\text{CS}_2/\text{CD}_2\text{Cl}_2$, $\delta(\text{CHDCl}_2) = 5.32$ ppm, at 10°C) with correlations from $^1\text{H}, ^{13}\text{C}$ -HSQC-, $^1\text{H}, ^{13}\text{C}$ -HMBC-, $^1\text{H}, ^1\text{H}$ -COSY- and $^1\text{H}, ^1\text{H}$ -ROESY-spectra.

Atom No.	$\delta ^1\text{H}$	$\delta ^{13}\text{C}$	Atom No.	$\delta ^1\text{H}$	$\delta ^{13}\text{C}$
1			8		143.8§
2		141.6§	81a	4.08§	41.4§
21	8.04	123.8	81b	4.93§	
22		130.6	9		
23		181.4	10		119.7
5		118.5	101		
51			102	8.22	128.6
52	8.43	129.4	103		151.2
53		151.8	1031		35.1
531		35.5	1032	1.47	31.9
532	1.87	32.2	104	7.85	123.1
54	7.98	123.2	105		151.2
55		151.6	1051		35.1
551		34.5	1052	1.42	31.9
552	1.07	31.7	106	8.15	128.6
56	7.80	127.3	11		
6			12		143.8§
7		143.8§	121a	4.06§	41.4
71a	4.10§	41.4	121b	4.96§	
71b	4.94§				

§: Tentatively assigned signals

Table S3: ^1H -NMR- and ^{13}C -NMR-signal assignment for **Ni₂-6**, minor conformer (500 MHz, 1:1 $\text{CS}_2/\text{CD}_2\text{Cl}_2$, $\delta(\text{CHDCl}_2) = 5.32$ ppm, at 10°C) with correlations from $^1\text{H}, ^{13}\text{C}$ -HSQC-, $^1\text{H}, ^{13}\text{C}$ -HMBC-, $^1\text{H}, ^1\text{H}$ -COSY- and $^1\text{H}, ^1\text{H}$ -ROESY-spectra.

Atom No.	$\delta ^1\text{H}$	$\delta ^{13}\text{C}$	Atom No.	$\delta ^1\text{H}$	$\delta ^{13}\text{C}$
1			8		143.8§
2		141.8§	81a	4.07§	41.4
21	8.18	123.9	81b	4.92§	
22		130.5	9		
23		181	10		119.8
5		118.5	101		
51			102	8.19	128.6
52	8.39	129.7	103		151.2
53		151.8	1031		35.1
531		35.5	1032	1.45	31.9
532	1.80	32.2	104	7.84	123.1
54	8.04	123.1	105		151.2
55		151.6	1051		35.1
551		34.5	1052	1.42	31.9
552	1.24	31.7	106	8.18	128.5
56	7.90	127.3	11		
6			12		143.8§
7		143.8§	121a	4.06§	41.4
71a	4.00§	41.4	121b	4.93§	
71b	4.92§				

§: Tentatively assigned signals

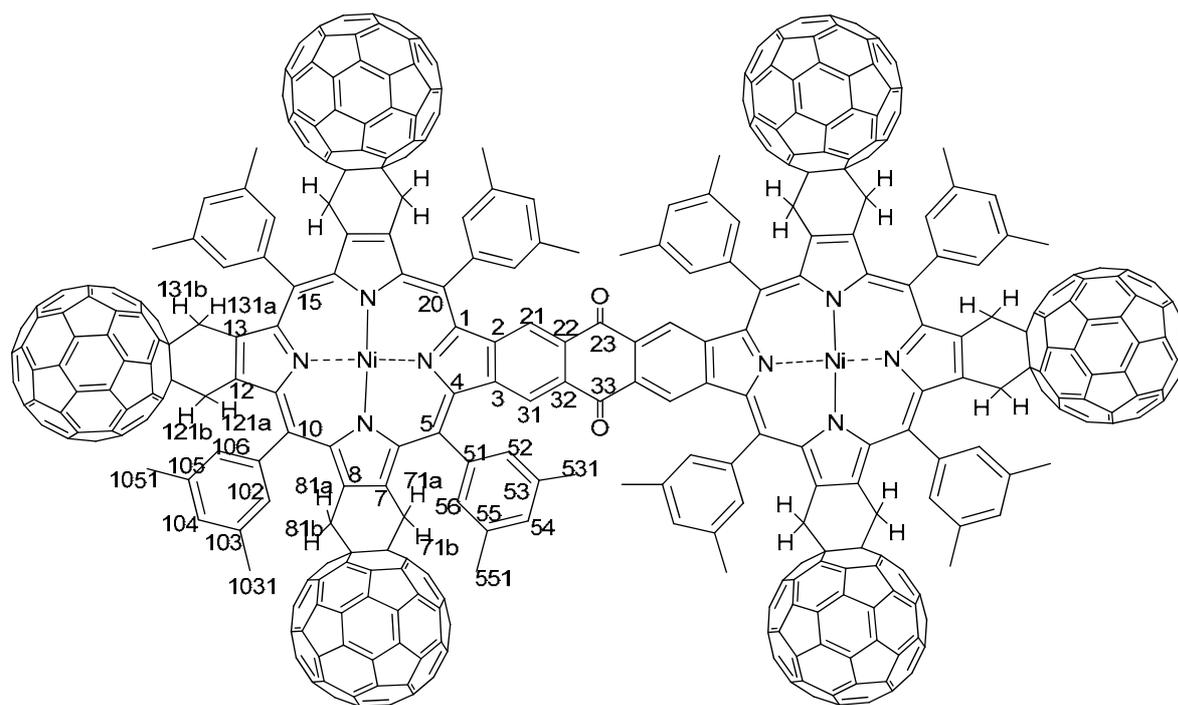


Figure S6. Atom numbering used here for Ni₂-6

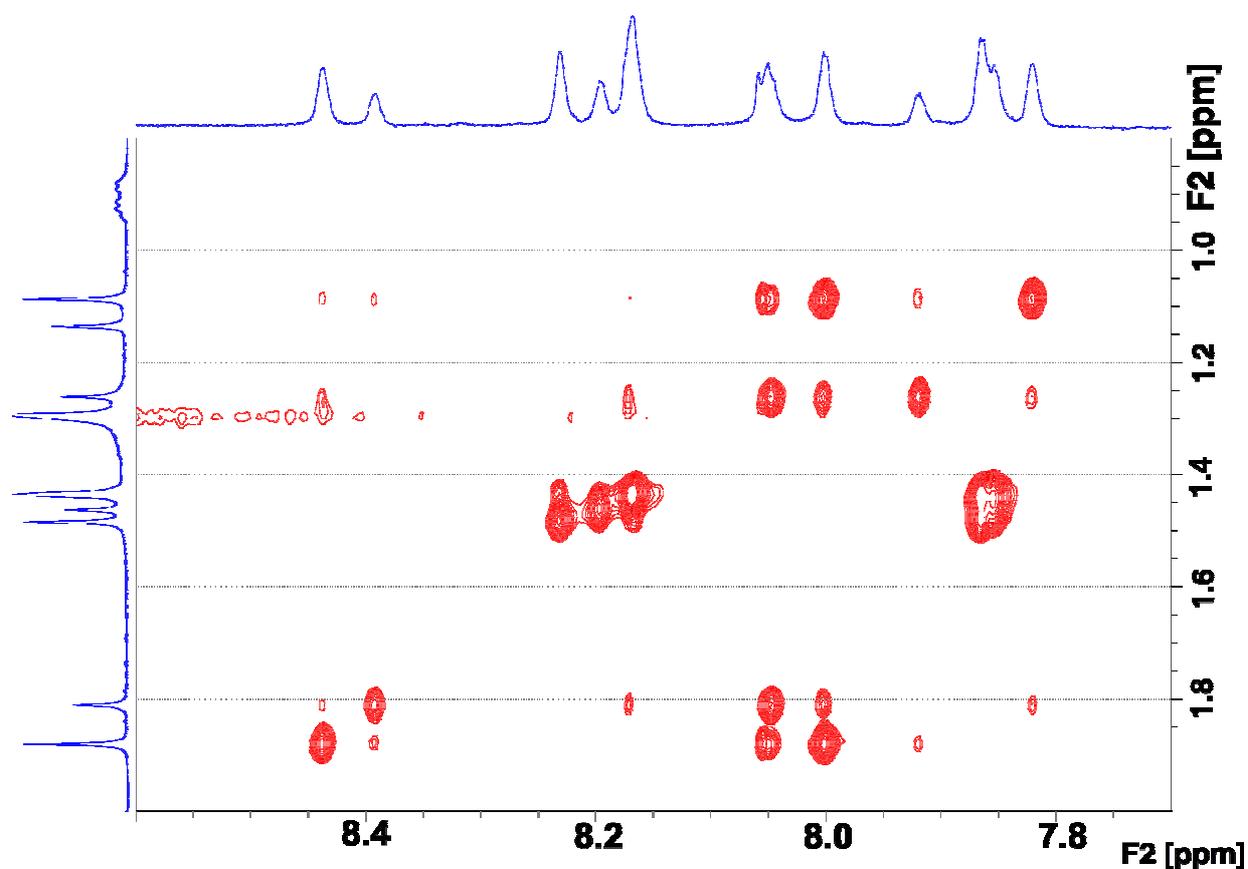


Figure S7. Section of a 500 MHz ¹H-ROESY-spectrum of Ni₂-6 in CS₂ / CD₂Cl₂ (1:1) at 25 °C showing intra-modular correlations of protons of the 3,5-di-*tert*-butyl-phenyl groups and weak cross-correlations due to conformational exchange

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