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Supporting Information

# A Molecular Nanotube with Three-Dimensional π-Conjugation**

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# Contents

## Synthesis

### General

Unless stated otherwise, all reagents were obtained from commercial sources and used as received without further purification. Diethyl ether and toluene were dried by passing over activated alumina. Diisopropylamine was dried by distillation over $CaH_2$. *N*-Bromosuccinimide was recrystallized from boiling water. 3,5-Trihexylsilylbromobenzene,[S1] hexakis-(4-[4-phenylpyridine])benzene[S2] (**T6**) and 5,15-bis[(triisopropylsilyl)ethynyl]porphyrin[S3] (**P1a**) were synthesized according to literature procedures.

NMR spectra were recorded on a Bruker AVII400, Bruker AVIII400 (400 MHz) or Bruker DRX500 (500 MHz) spectrometer. The residual solvent peak was used as internal reference (chloroform, $^1$H δ = 7.26 ppm, $^{13}$C δ = 77.2 ppm. Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constant(s) were reported whenever possible

Analytical gel permeation chromatography (GPC) was performed on a JAIGEL H-P pre-column, a JAIGEL 3H-A (8 mm × 500 mm) and a JAIGEL 4H-A column (8 mm × 500 mm) in series with toluene/pyridine 100/1 as eluent or on two PLgel 3 µm Mixed-E columns (2 × 300 mm length, 7.5 mm diameter) and two PLgel 5 µm Mixed-D columns (3 × 300 mm length, 7.5 mm diameter) in series with THF as an eluent. Preparative recycling GPC was performed on a JAIGEL H-P pre-column, a JAIGEL 3H (20 mm × 600 mm) and a JAIGEL 4H column (20 mm × 600 mm) in series with toluene/pyridine 100/1 as eluent.

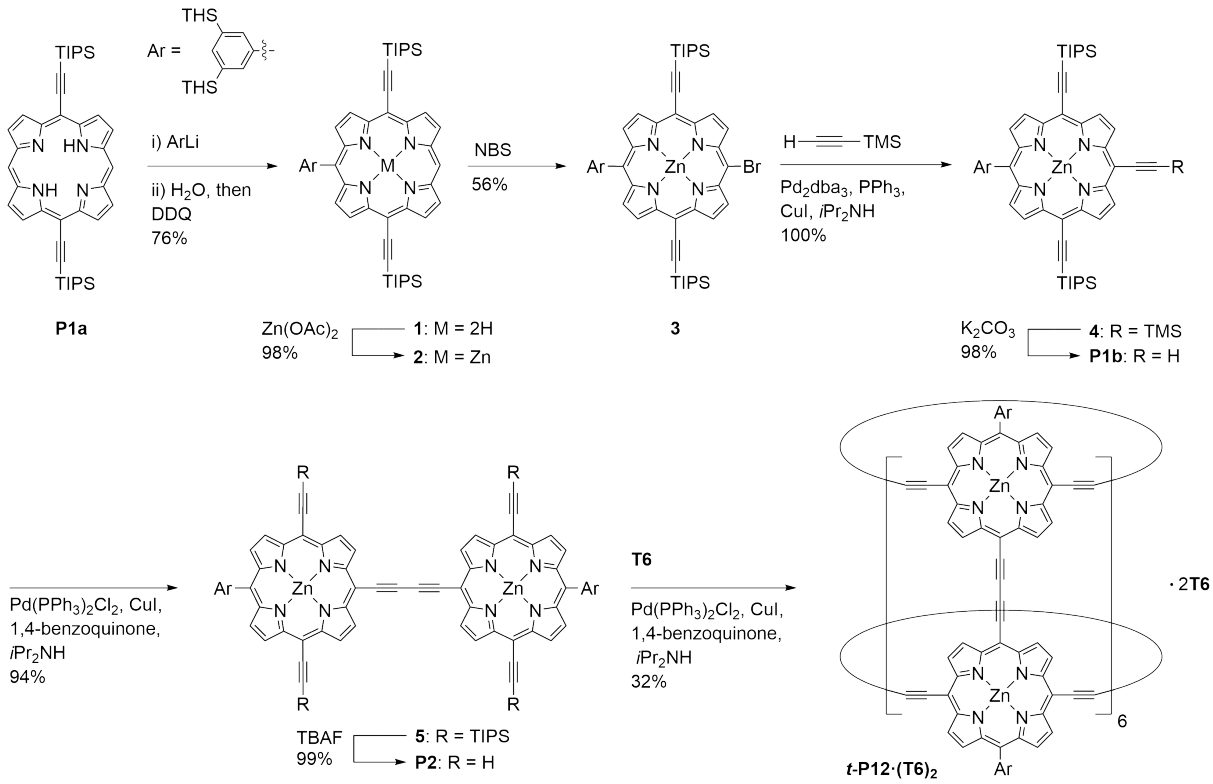



**Figure S1.** Synthesis of nanotube ***t*-P12·(T6)$_2$.**

### Free-base porphyrin 1

To a solution of 3,5-trihexylsilylbromobenzene (0.65 g, 0.90 mmol) in $Et_2O$ (5 mL) at –78 °C under $N_2$ atmosphere was added dropwise *n*-BuLi (1.6 M in hexanes, 0.56 mL, 0.90 mmol). The mixture was warmed to room temperature and stirred for 1 h. This solution was added dropwise to a solution of **P1a** (100 mg, 0.15 mmol) in THF (5 mL). The mixture was stirred at room temperature overnight. Water (0.5 mL) was added, followed by DDQ (102 mg, 0.45 mmol). The reaction mixture was stirred

for 20 min before addition of $Et_3N$ (0.2 mL). The volatiles were removed *in vacuo* and the residue was taken up in $CH_2Cl_2$ (50 mL) and washed with $H_2O$ (2 × 30 mL). The organic layer was dried over $Na_2SO_4$ and concentrated. Column chromatography (9:1 PE:$CH_2Cl_2$) afforded **1** (0.15 g, 0.11 mmol, 76%) as a purple solid. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 10.06 (s, 1H), 9.75 (d, *J* = 4.4 Hz, 2H), 9.68 (d, *J* = 4.8 Hz, 2H), 9.29 (d, *J* = 4.4 Hz, 2H), 8.85 (d, *J* = 4.8 Hz, 2H), 8.25 (s, 2H), 8.02 (s, 1H), 1.55–1.45 (54H), 1.45–1.36 (m, 12H), 1.36–1.29 (m, 24H), 0.98–0.92 (m, 12H), 0.92–0.87 (m, 18H), –2.36 (s, 2H). **$^{13}$C NMR ($CDCl_3$, 125 MHz)**: 149.4 (4C α-pyrrole), 146.4 (4C α-pyrrole), 140.4 (2CH *o*-Ar), 140.2 (CH *p*-Ar), 139.7 (C *ipso*-Ar), 135.2 (2C *m*-Ar), 132.4 (2C β-pyrrole), 131.7 (2C β-pyrrole), 130.9 (2C β-pyrrole), 130.2 (2C β-pyrrole), 123.7 (C *meso*), 108.6 (CH *meso*), 106.3 (2C *meso*), 100.8 (2C C≡C), 99.5 (2C C≡C), 33.7 ($6CH_2$ $Si(CH_3)_3$), 31.8 ($6CH_2$ $Si(CH_3)_3$), 24.3 ($6CH_2$ $Si(CH_3)_3$), 22.8 ($6CH_2$ $Si(CH_3)_3$), 19.2 ($12CH_3$ TIPS), 14.3 ($6CH_3$ $Si(CH_3)_3$), 12.9 (6CH TIPS), 12.1 ($6CH_2$ $Si(CH_3)_3$). **MS (MALDI)** calcd. for $C_{84}H_{134}N_4Si_4Zn$: 1310.97, found: 1311.16.

**Zinc porphyrin 2**

To a solution of **1** (0.15 g, 0.11 mmol) in $CHCl_3$ (5 mL) was added a solution of zinc acetate dihydrate (0.11 g, 0.50 mmol) in MeOH (1 mL). The mixture was stirred at room temperature for 1 h before filtration over a short silica plug (100:1 $CH_2Cl_2$:pyridine). Compound **2** (1:1 complex with pyridine, 164 mg, 98%) was obtained as a purple solid. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 10.04 (s, 1H), 9.81 (d, *J* = 4.4 Hz, 2H), 9.73 (d, *J* = 4.4 Hz, 2H), 9.31 (d, *J* = 4.0 Hz, 2H), 8.87 (d, *J* = 4.4 Hz, 2H), 8.23 (s, 2H), 7.99 (s, 1H), 1.55–1.44 (54H), 1.44–1.35 (m, 12H), 1.35–1.29 (m, 24H), 0.97–0.91 (m, 12H), 0.91–0.86 (m, 18H). **$^{13}$C NMR ($CDCl_3$, 100 MHz)**: 152.6 (2C), 152.4 (2C), 150.2 (2C), 150.0 (2C), 141.2 (C), 140.4 (2CH), 139.2 (CH), 134.6 (2C), 132.8 (2CH), 132.2 (2CH), 131.6 (2CH), 130.8 (2CH), 124.2 (C), 110.4 (CH), 107.1 (2C), 100.6 (2C), 97.3 (2C), 33.7 ($6CH_2$), 31.8 ($6CH_2$), 24.2 ($6CH_2$), 22.8 ($6CH_2$), 19.3 ($12CH_3$), 14.3 ($6CH_3$), 12.9 (6CH), 12.1 ($6CH_2$). **MS (MALDI)** calcd. for $C_{84}H_{132}N_4Si_4Zn$: 1372.88, found: 1373.26.

**Bromide-substituted porphyrin 3**

To a solution of **2** (164 mg, 0.11 mmol) in $CHCl_3$ (5 mL) and pyridine (0.5 mL) was added *N*-bromosuccinimide (21 mg, 0.12 mmol). The mixture was stirred overnight at room temperature. TLC (4:1 petrol:$CH_2Cl_2$, $R_f \approx 0.45$, starting material is fluorescent while product is not) indicated the presence of starting material and additional NBS (2 × 10 mg) was added until the reaction was complete. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (4:1 PE:$CH_2Cl_2$, + 1% pyridine) yielding **3** (97 mg, 0.067 mmol, 56%) as purple solid. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 9.77 (d, *J* = 4.4 Hz, 2H), 9.71 (d, *J* = 4.4 Hz, 2H), 9.69 (d, *J* = 4.4 Hz, 2H), 8.84 (d, *J* = 4.4 Hz, 2H), 8.22 (s, 2H), 8.02 (s, 1H), 1.59–1.47 (54H), 1.47–1.38 (m, 12H), 1.38–1.32 (m, 24H), 1.02–0.95 (m, 12H), 0.95–0.90 (m, 18H).**$^{13}$C NMR (CDCl3, 125 MHz)**: 152.8 (2C), 152.7 (2C), 151.0 (2C), 149.6 (2C), 140.7 (C), 140.2 (2CH), 139.2 (CH), 134.8 (2C), 133.3 (2C), 133.1 (2C), 132.2 (2C), 131.3 (2C), 124.5 (C), 109.8 (C), 106.0 (2C), 101.9 (2C), 98.2 (2C), 33.7 ($6CH_2$), 31.7 ($6CH_2$), 24.1 ($6CH_2$), 22.7 ($6CH_2$), 19.2 ($12CH_3$), 14.3 ($6CH_3$), 12.8 (6CH), 12.1 ($6CH_2$). **MS (MALDI)** calcd. for $C_{84}H_{13}BrN_4Si_4Zn$: 1453.79, found: 1453.12.

**Tris alkyne-substituted porphyrin 4**

In a 25-mL two-necked flask were placed **3** (97 mg, 0.067 mmol), $Pd_2dba_3$ (6.4 mg, 0.007 mmol), CuI (1.3 mg, 0.007 mmol) and triphenylphosphine (3.7 mg, 0.014 mmol). Toluene (4 mL) and *N*,*N*-diisopropylamine (2 mL) were added and the mixture was deoxygenated by freeze-pump-thaw cycles. Trimethylsilylacetylene (14 μL, 0.1 mmol) was added and the reaction mixture was stirred overnight at room temperature. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (5:1 PE:$CH_2Cl_2$, + 1% pyridine) yielding **4** (98 mg, 0.067 mmol, 100%) as a purple solid. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 9.76 (d, *J* = 4.4 Hz, 2H), 9.71 (d, *J* = 4.4 Hz, 2H), 9.65 (d, *J* = 4.4 Hz, 2H), 8.80 (d, *J* = 4.4 Hz, 2H), 8.21 (s, 2H), 8.01 (s, 1H), 1.59–1.46 (54H), 1.47–1.38 (m, 12H), 1.38–1.30 (m, 24H), 1.00–0.94 (m, 12H), 0.94–0.89 (m, 18H), 0.69 (s, 9H). **$^{13}$C NMR ($CDCl_3$, 100 MHz)**: 152.6 (2C), 152.5 (2C), 152.3 (2C), 150.1 (2C), 140.7 (C), 140.1 (2CH), 139.1 (CH), 134.7 (2C), 132.9 (2CH), 131.8 (2CH), 131.5 (2CH), 130.6 (2CH), 125.6 (C), 109.8 (C), 108.0 (2C), 102.0 (2C), 100.6 (C), 100.3 (C), 97.8 (2C), 33.5 ($6CH_2$), 31.6 ($6CH_2$), 24.1 ($6CH_2$), 22.6 ($6CH_2$), 19.1

($12CH_3$), 14.2 ($6CH_3$), 12.7 (6CH), 12.0 ($6CH_2$), 0.5 ($3CH_3$). **MS (MALDI)** calcd. for $C_{89}H_{140}N_4Si_5Zn$: 1469.92, found: 1467.8.

**Free alkyne P1b**

To a solution of **4** (280 mg, 0.190 mmol) in THF (12 mL) and MeOH (12 mL) was added $K_2CO_3$ (262 mg, 1.90 mmol). The suspension was stirred at 20 °C for 30 min before removal of the volatiles *in vacuo*. The residue was taken up in $CH_2Cl_2$ (30 mL) and washed with $H_2O$ (2 × 30 mL). The organic layer was dried over $Na_2SO_4$ and concentrated. The residue was subjected to column chromatography (6:1 PE:$CH_2Cl_2$ +1% pyridine) yielding **P1b** (261 mg, 0.186 mmol, 98%) as a green-purple solid. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 9.73 (d, *J* = 4.6 Hz, 2H), 9.69 (d, *J* = 4.6 Hz, 2H), 9.62 (d, *J* = 4.6 Hz, 2H), 8.78 (d, *J* = 4.6 Hz, 2H), 8.17 (s, 2H), 7.96 (s, 1H), 4.16 (s, 1H), 1.55–1.41 (m, 54H), 1.41–1.33 (m, 12H), 1.33–1.25 (m, 24H), 0.95–0.89 (m, 12H), 0.89–0.83 (m, 18H); **$^{13}$C NMR ($CDCl_3$, 125 MHz)**: 152.8 (2C), 152.6 (2C), 152.5 (2C), 150.2 (2C), 140.7 (C), 140.2 (2CH), 139.3 (CH), 134.8 (2C), 133.1 (2CH), 132.1 (2CH), 131.5 (2CH), 130.8 (2CH), 125.8 (C), 109.8 (2C), 102.1 (CH), 99.1 (C), 98.1 (C), 86.5 (C), 83.2 (C), 33.7 ($6CH_2$), 31.7 ($6CH_2$), 24.2 ($6CH_2$), 22.8 ($6CH_2$), 19.3 ($12CH_3$), 14.3 ($6CH_3$), 12.8 (6CH), 12.1 ($6CH_2$). **MS (MALDI)** calcd. for $C_{86}H_{132}N_4Si_4Zn$: 1398.88, found: 1397.86.

**Dimer 5**

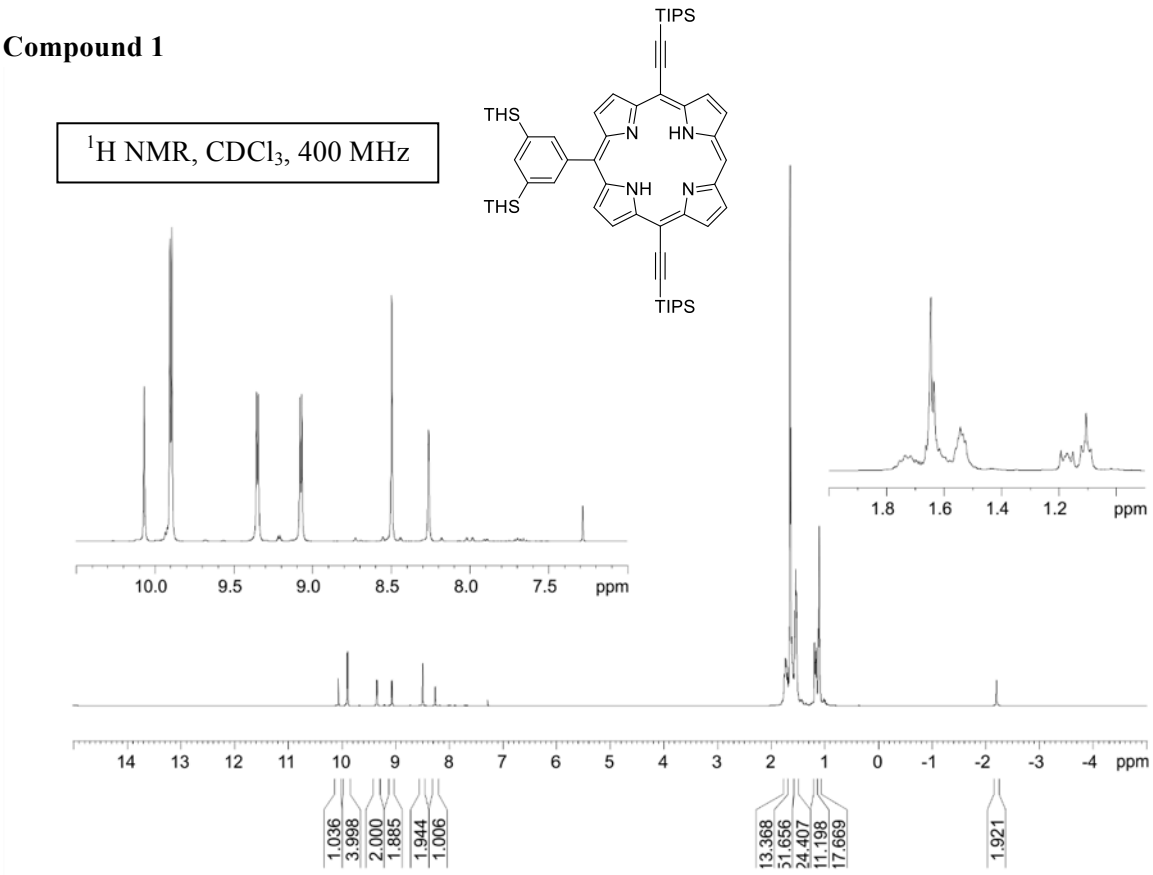
To a solution of **P1b** (261 mg, 0.186 mmol) in dry toluene (5 mL) and diisopropylamine (5 mL) was added $Pd(PPh_3)_2Cl_2$ (6.3 mg, 9 µmol), CuI (17 mg, 0.09 mmol) and 1,4-benzoquinone (41 mg, 0.38 mmol). The mixture was stirred at 20 °C for 4 h before removal of the volatiles *in vacuo*. The residue was passed through a short silica column (4:1 PE:$CH_2Cl_2$ +1% pyridine) and subsequently purified by size-exclusion chromatography (BioBeads SX-1, toluene) yielding **5** (246 mg, 0.088 mmol, 94%) as a green-purple solid. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 9.98 (d, *J* = 4.6 Hz, 4H), 9.86 (d, *J* = 4.6 Hz, 4H), 9.64 (d, *J* = 4.6 Hz, 4H), 8.80 (d, *J* = 4.6 Hz, 4H), 8.21 (s, 4H), 8.00 (s, 2H), 1.60–1.45 (m, 108H), 1.45–1.36 (m, 24H), 1.36–1.29 (m, 48H), 0.99–0.92 (m, 24H), 0.92–0.87 (m, 36H). **MS (MALDI)** calcd. for $C_{172}H_{262}N_8Si_8Zn_2$: 2796.75, found: 2794.58. **UV/vis/NIR (chloroform)** $\lambda_{max}$ (log ε): 459 (5.43), 482 (5.32), 514 (5.42), 664 (4.75), 705 (4.85).

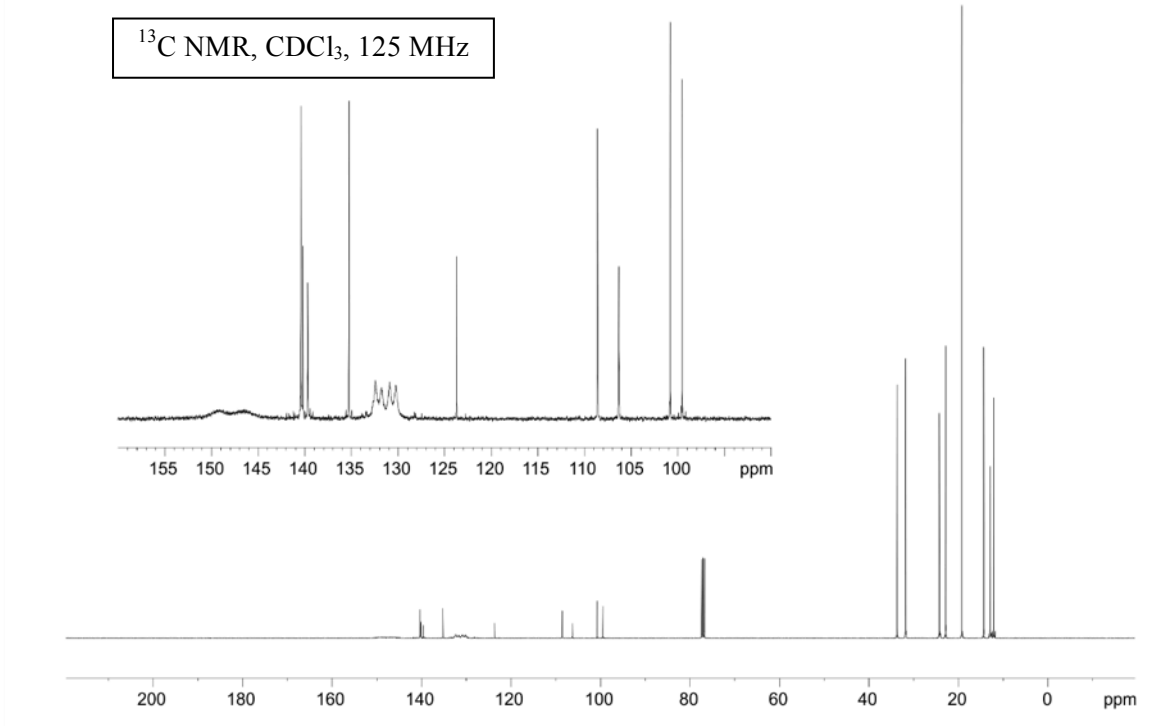
**Deprotected dimer P2 and *t*-P12·(T6)$_2$**

To a solution of **5** (42 mg, 0.015 mmol) in $CH_2Cl_2$ (8 mL) was added TBAF (0.15 mL of a 1.0 M solution in THF, 0.15 mmol). The solution was stirred at 20 °C for 30 min and then directly passed through a silica plug ($CH_2Cl_2$ +1% pyridine) yielding crude **P2** (~35 mg) after evaporation. This was used in the next step without further purification. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 9.96 (d, *J* = 4.6 Hz, 4H), 9.81 (d, *J* = 4.6 Hz, 4H), 9.61 (d, *J* = 4.6 Hz, 4H), 8.82 (d, *J* = 4.6 Hz, 4H), 8.21 (s, 4H), 7.98 (s, 2H), 4.20 (s, 4H), 1.55–143 (m, 24H), 1.42–1.33 (m, 24H), 1.33–1.26 (m, 48H), 0.96–0.90 (m, 24H), 0.90–0.85 (m, 36H). Crude **P2** was dissolved in $CHCl_3$ (~10 mL) and hexakis-(4-[4-phenylpyridine])benzene (**T6**) (23.7 mg, 0.024 mmol) was added. After stirring for 5 min, a UV/vis absorption spectrum was recorded to check formation of the complex. The solution was concentrated and the residue re-dissolved in dry toluene (10 mL) and diisopropylamine (5 mL). The solution was heated to 65 °C and subsequently $Pd(PPh_3)_2Cl_2$ (2.1 mg, 3 µmol), CuI (2.9 mg, 1.5 µmol) and 1,4-benzoquinone (3.2 mg, 0.030 mmol) were added. Heating was continued for 2.5 h, and then the reaction mixture was allowed to cool before loading directly onto a silica plug and eluted with toluene. After removal of the volatiles *in vacuo*, the residue was passed through a second silica plug with $CH_2Cl_2$. The material was further purified by size-exclusion chromatography (BioBeads SX-1, toluene) and finally subjected to recycling GPC yielding ***t*-P12·(T6)$_2$** (12 mg, 0.8 µmol, 32%) as a purple-pink solid. **$^1$H NMR ($CDCl_3$, 400 MHz)**: 9.95 (d, *J* = 4.2 Hz, 24H), 9.91 (d, *J* = 4.2 Hz, 24H), 9.38 (d, *J* = 4.2 Hz, 24H), 8.60 (d, *J* = 4.2 Hz, 24H), 8.21 (s, 12H), 7.96 (s, 12H), 7.93 (s, 12H), 5.60–5.45 (m, 48H), 5.11 (d, *J* = 5.9 Hz, 24H), 2.64 (d, *J* = 5.9 Hz, 24H), 1.45–1.36 (m, 144H), 1.36–1.29 (m, 144H), 1.29–1.18 (m, 288H), 0.95–0.82 (m, 216H), 0.82–0.71 (m, 144H). **MS (MALDI-TOF)** calculated for $C_{960}H_{1164}N_{60}Si_{24}Zn_{12}$: 14994; found: 15036. **UV/vis/NIR (toluene)** $\lambda_{max}$ (log *ε*): 528 (5.89), 791 (5.60), 831 (5.72), 873 (5.71).

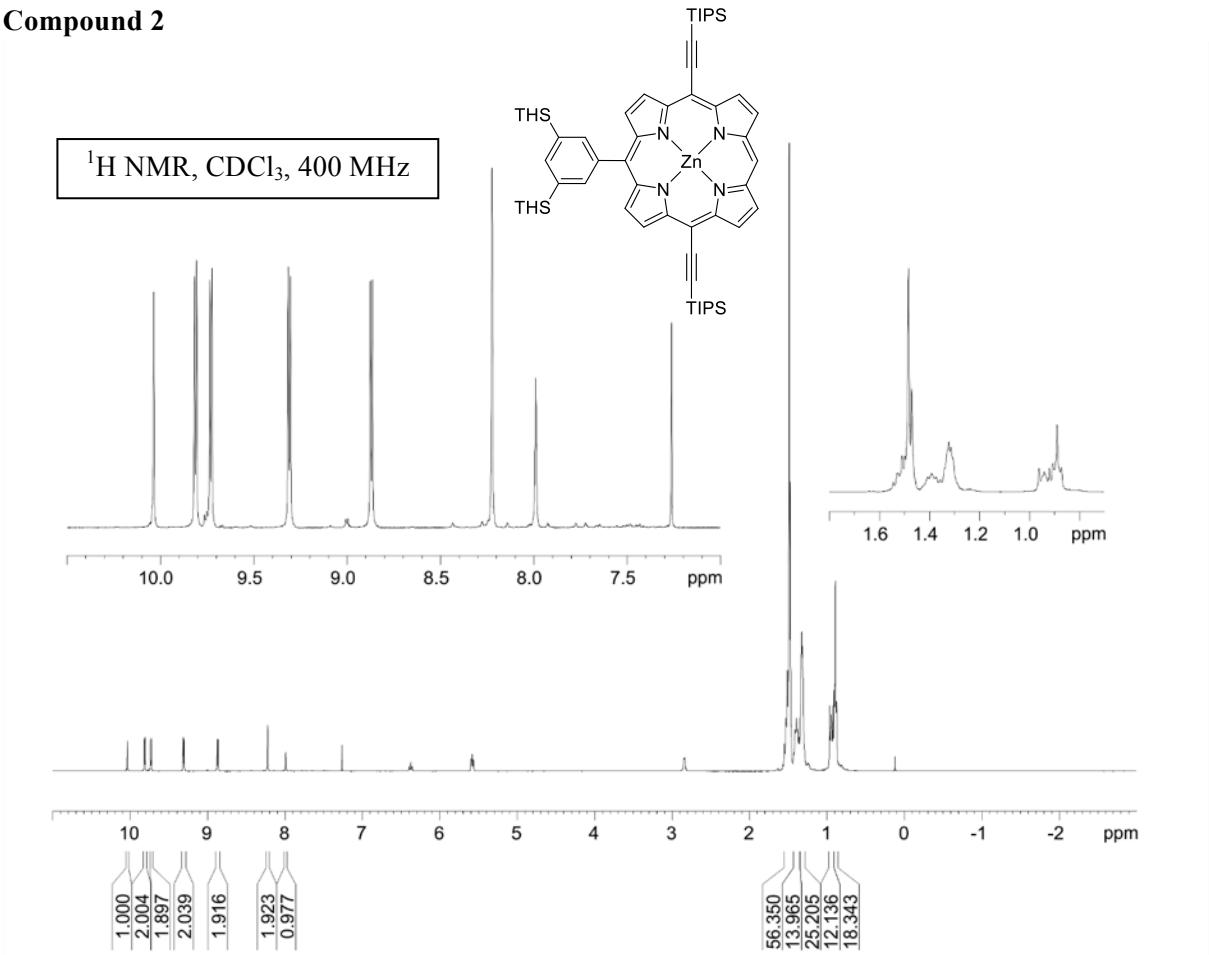
## NMR Spectra

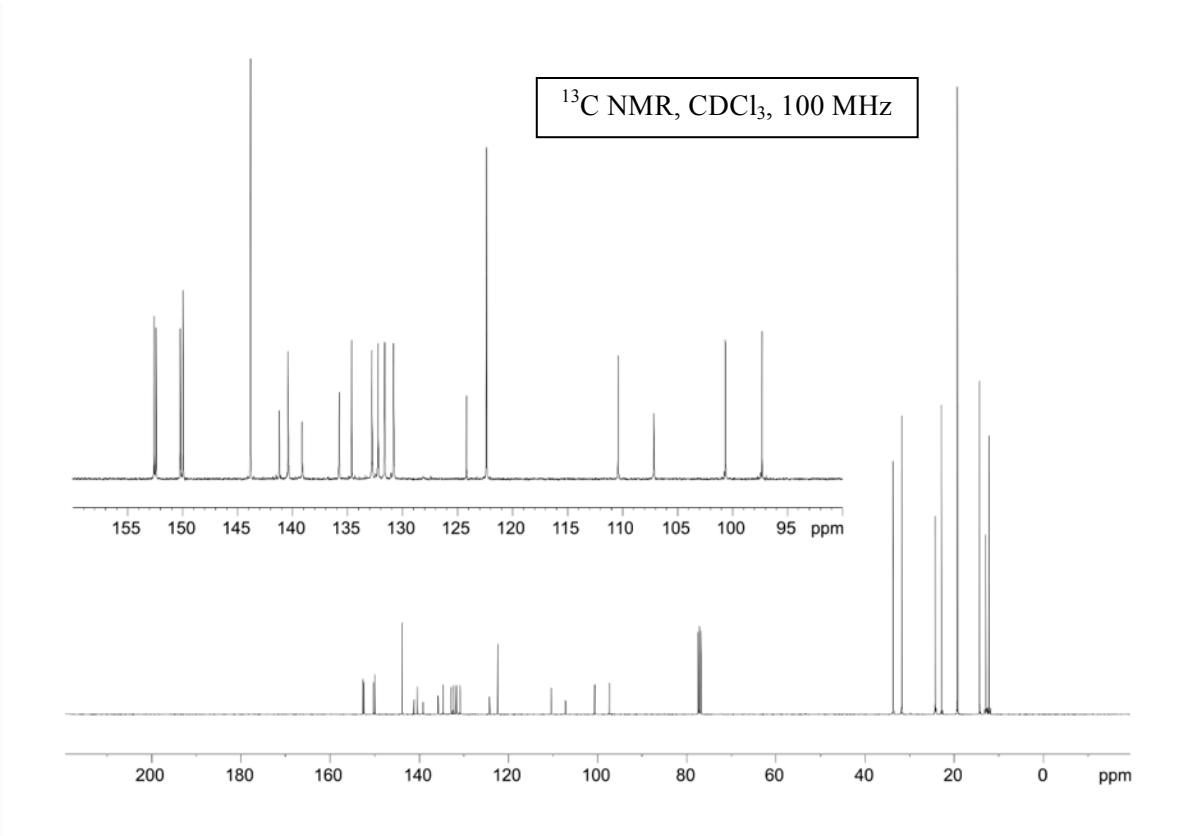
### Compound 1



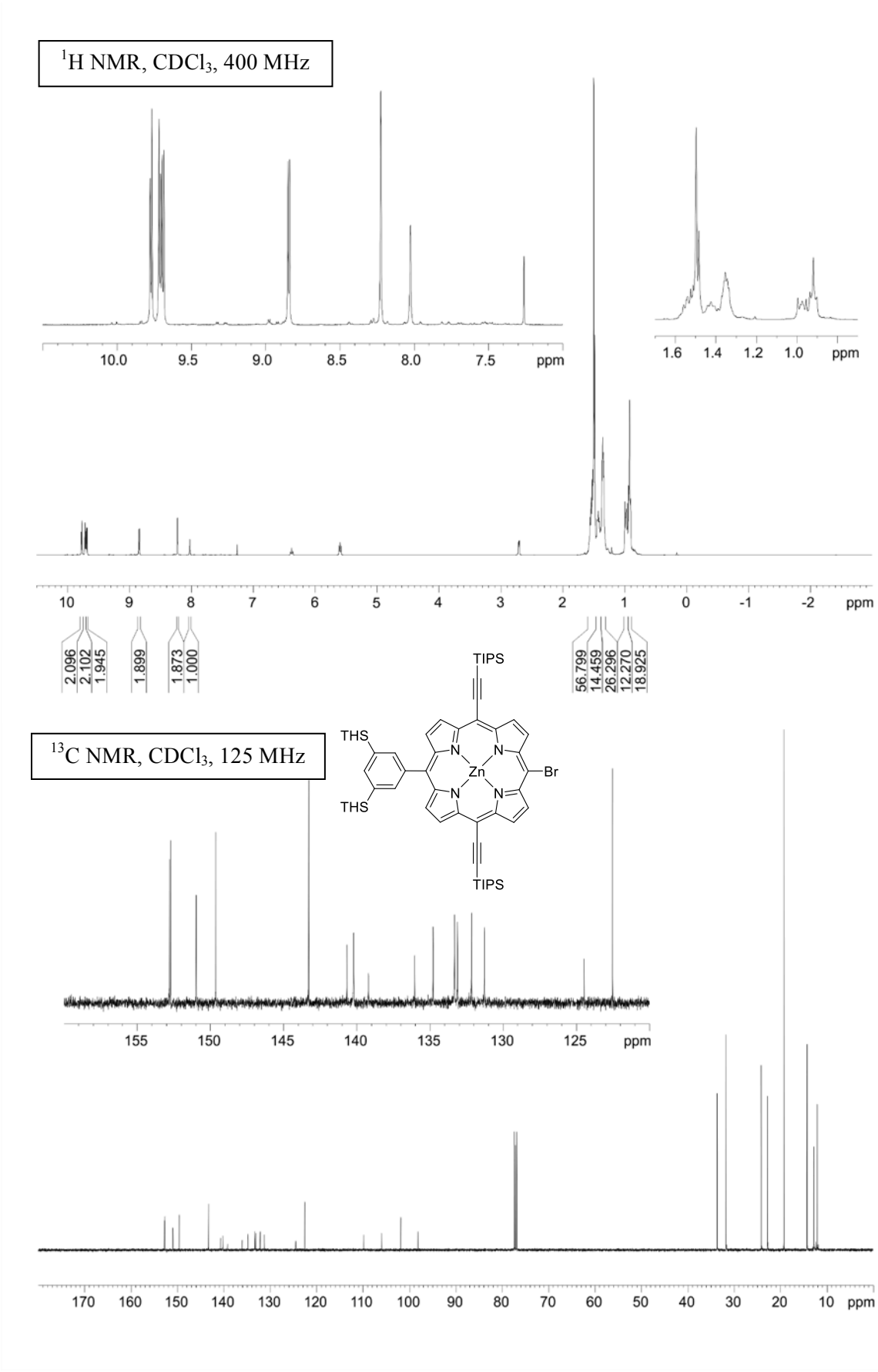



**Compound 2**

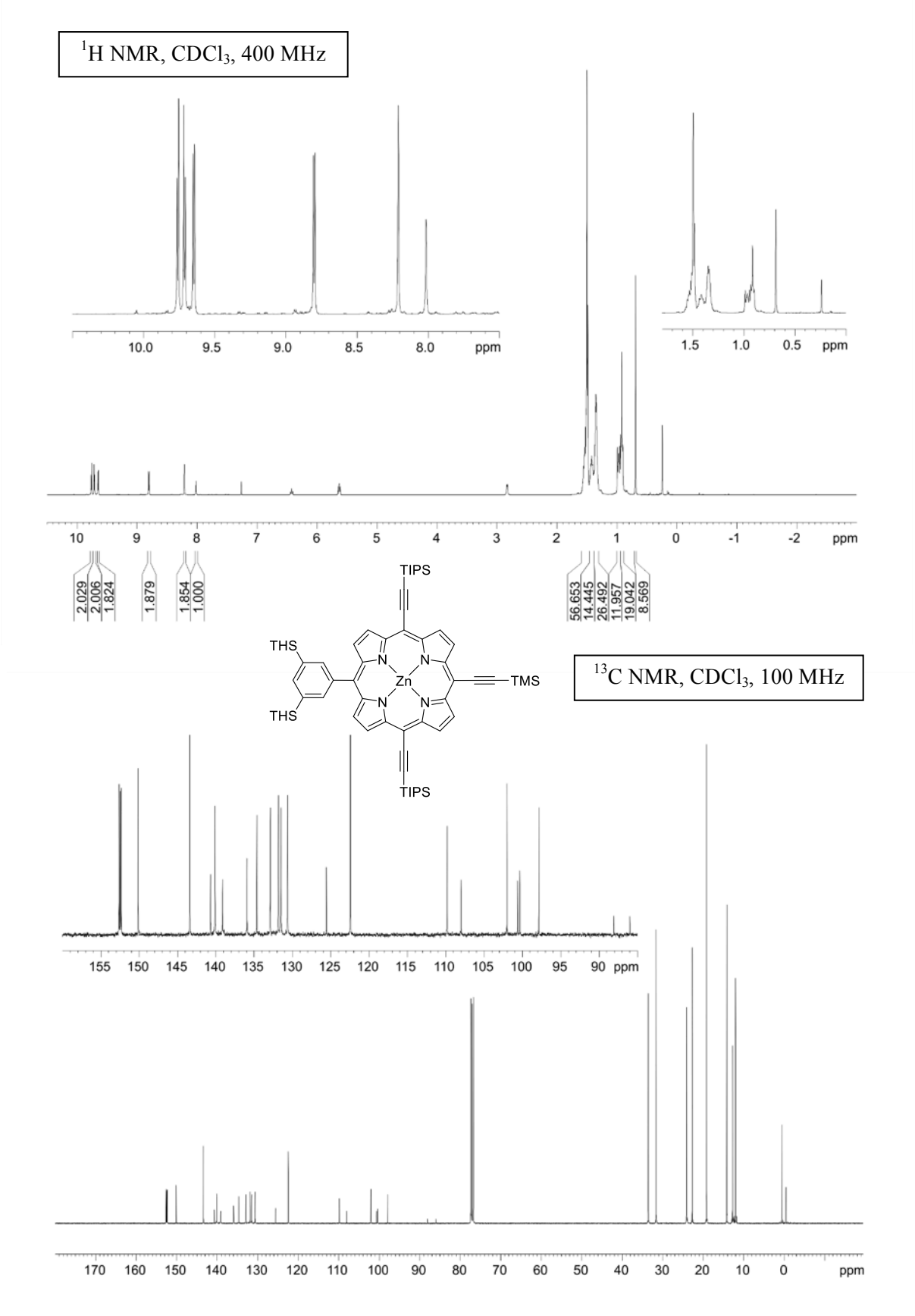

TIPS
THS
THS
N
N
Zn
N
N
TIPS
$^{1}$H NMR, $CDCl_3$, 400 MHz
10.0 9.5 9.0 8.5 8.0 7.5 ppm
1.6 1.4 1.2 1.0 ppm
10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
1.000 2.004 1.897 2.039 1.916 1.923 0.977
56.350 13.965 25.205 12.136 18.343


$^{13}$C NMR, $CDCl_3$, 100 MHz
155 150 145 140 135 130 125 120 115 110 105 100 95 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

**Compound 3**


$^{1}$H NMR, $CDCl_3$, 400 MHz
10.0 9.5 9.0 8.5 8.0 7.5 ppm
1.6 1.4 1.2 1.0 ppm
10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
2.096 2.102 1.945 1.899 1.873 1.000 56.799 14.459 26.296 12.270 18.925
TIPS
THS
THS
N
N
Zn
N
N
Br
TIPS
$^{13}$C NMR, $CDCl_3$, 125 MHz
155 150 145 140 135 130 125 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

**Compound 4**


$^1$H NMR, $CDCl_3$, 400 MHz
10.0 9.5 9.0 8.5 8.0 ppm
1.5 1.0 0.5 ppm
10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
2.029 2.006 1.824 1.879 1.854 1.000 56.653 14.445 26.492 11.957 19.042 8.569
TIPS
THS
THS
N
N
Zn
N
N
TMS
TIPS
$^{13}$C NMR, $CDCl_3$, 100 MHz
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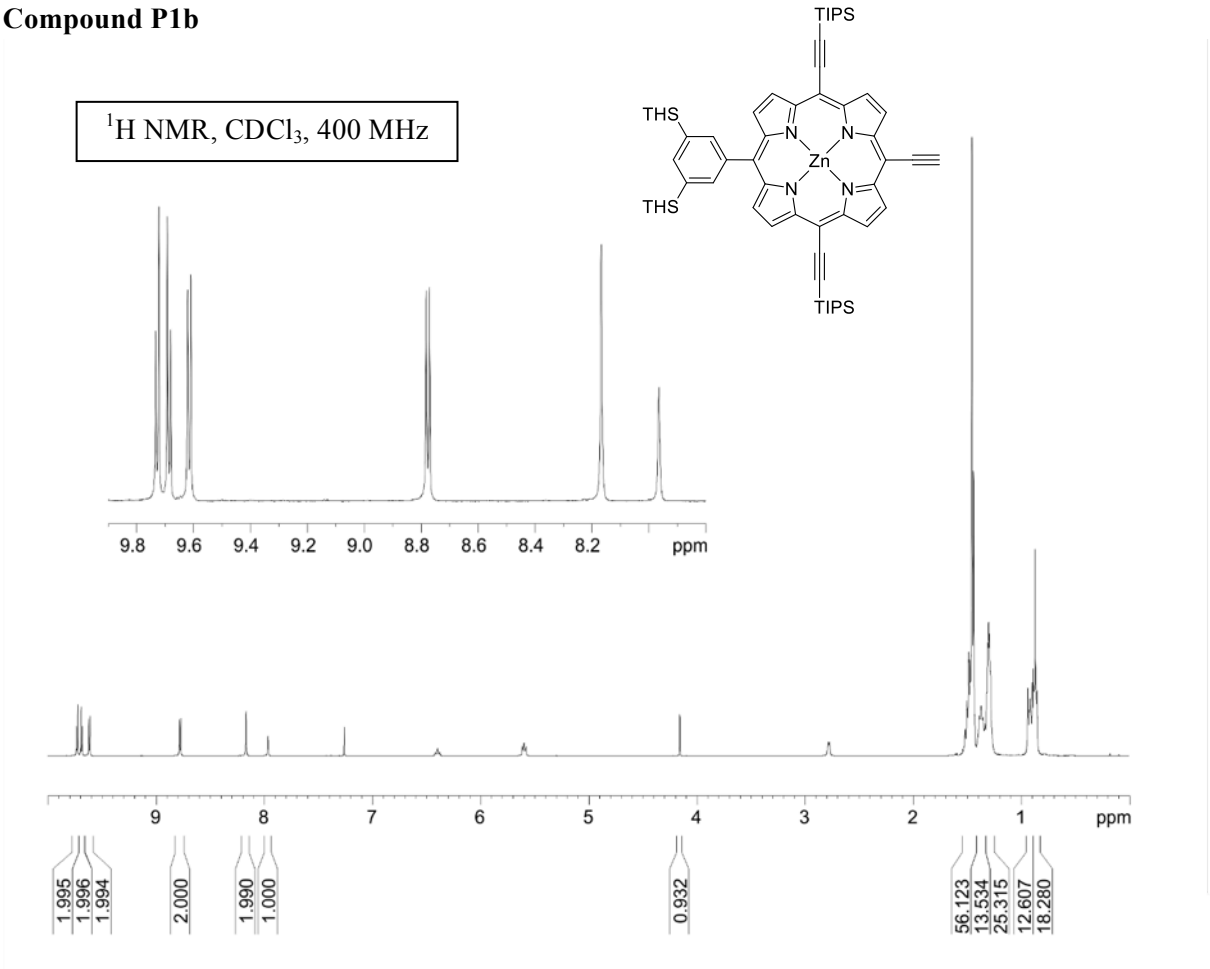
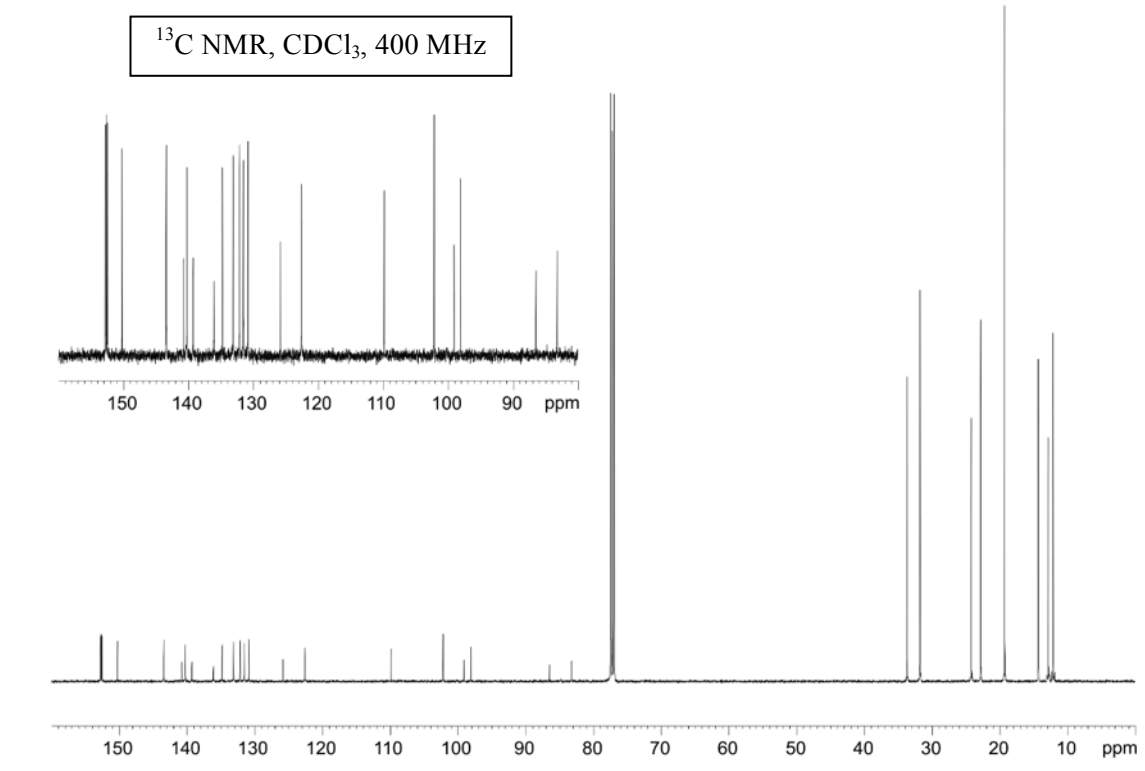
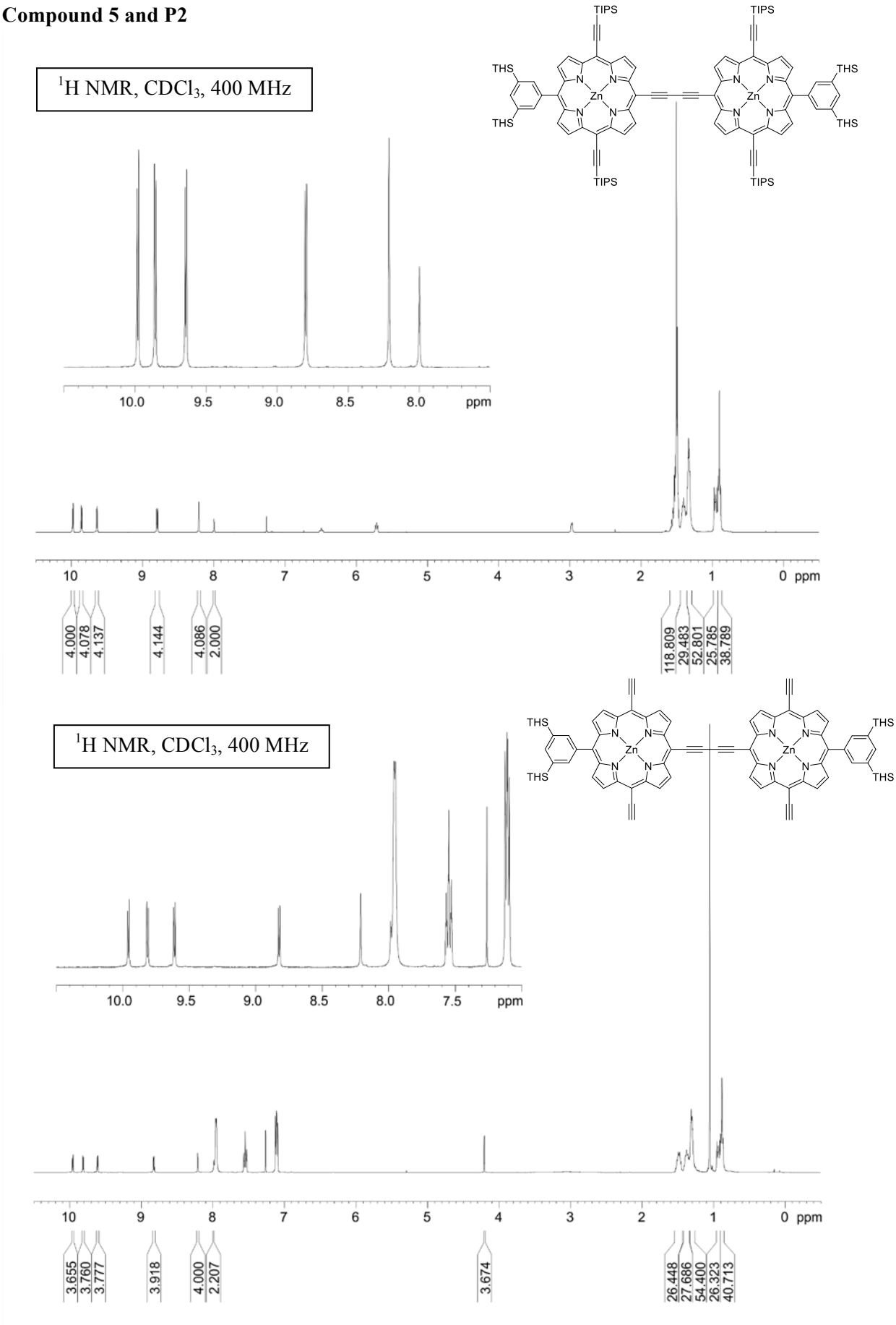
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

**Compound P1b**



**Compound 5 and P2**



***t*-P12·(T6)$_2$**

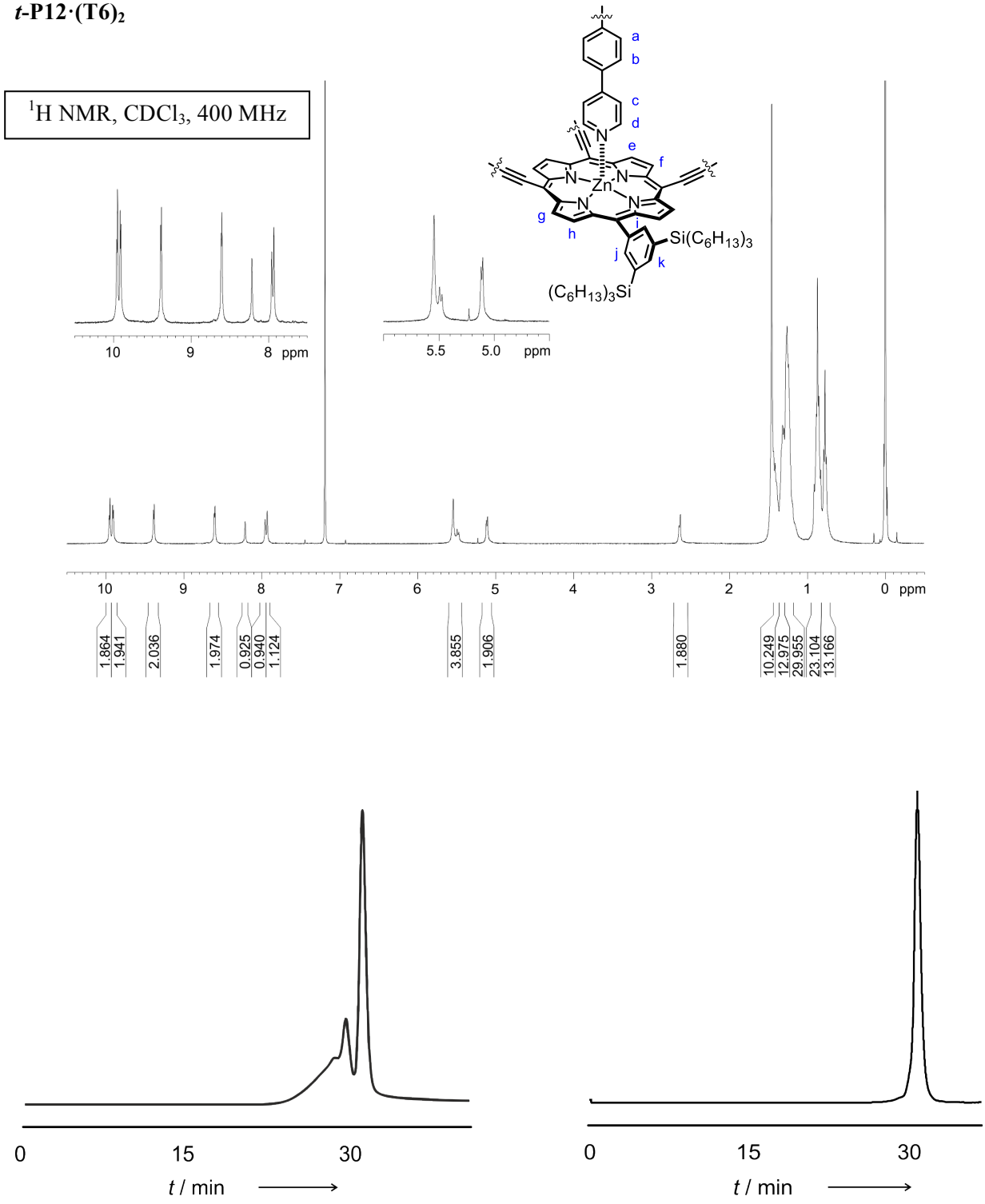



**Figure S2.** GPC (THF) trace of ***t*-P12·(T6)$_2$** before (left) and after (right) purification by recycling GPC. Detection wavelength: 529 nm. Column: two PLgel 3 µm Mixed-E columns (2 × 300 mm length, 7.5 mm diameter) and two PLgel 5 µm Mixed-D columns (3 × 300 mm length, 7.5 mm diameter) in series.

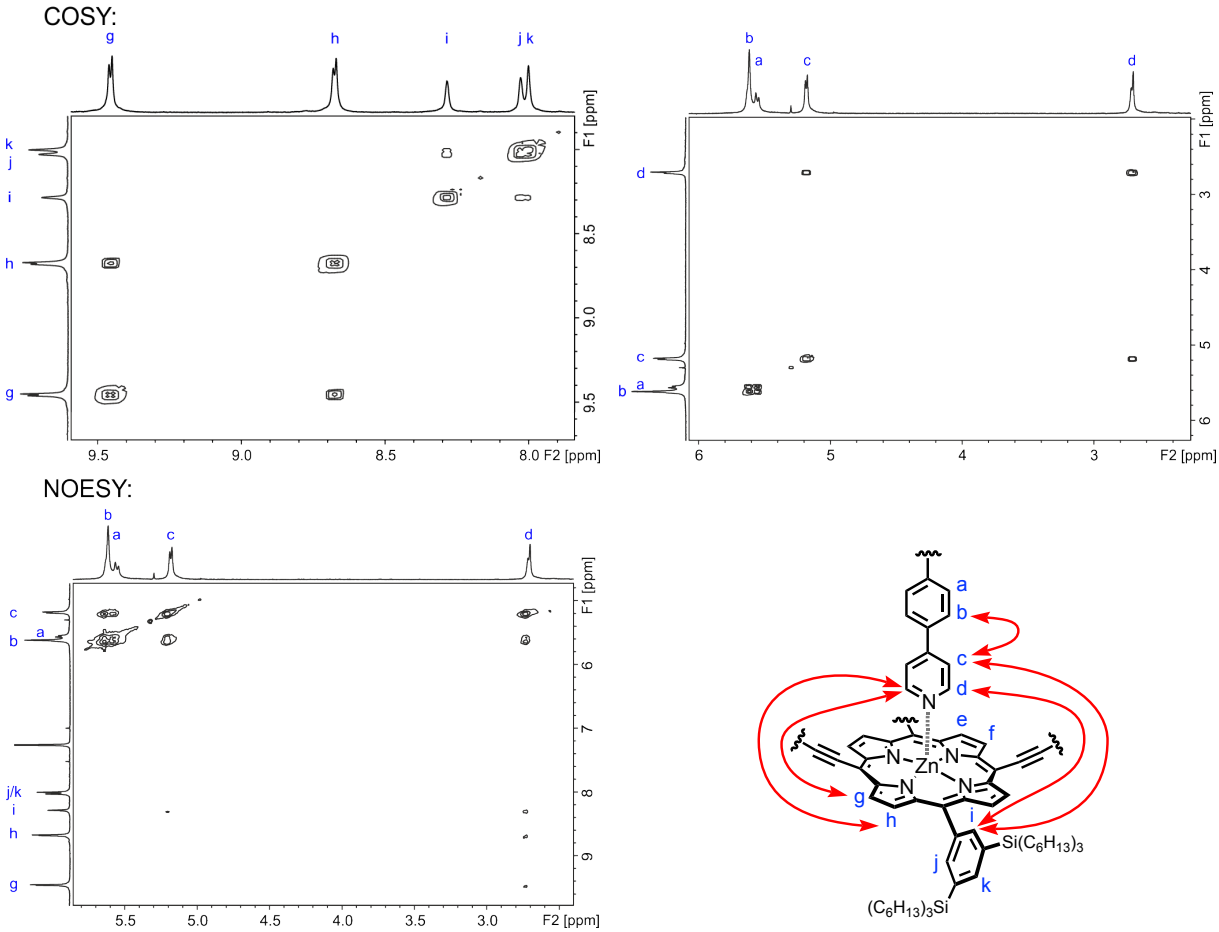



**Table S1.** Overview of COSY interactions

| | a | b | c | d | g | h | i | j | k |
|---|---|---|---|---|---|---|---|---|---|
| a | ■ | + | | | | | | | |
| b | + | ■ | | | | | | | |
| c | | | ■ | + | | | | | |
| d | | | + | ■ | | | | | |
| g | | | | | ■ | + | | | |
| h | | | | | + | ■ | | | |
| i | | | | | | | ■ | + | + |
| j | | | | | | | + | ■ | |
| k | | | | | | | + | | ■ |

**Table S2.** Overview of NOESY interactions

| | a | b | c | d | g | h | i | j | k |
|---|---|---|---|---|---|---|---|---|---|
| a | ■ | | s | w | | | | | |
| b | | ■ | s | s | | | | | |
| c | s | s | ■ | s | | | w | | |
| d | w | s | s | ■ | w | w | w | | |
| g | | | | w | ■ | s | w | w | |
| h | | | | w | s | ■ | s | s | w |
| i | | | w | w | w | s | ■ | w | w |
| j | | | | | w | s | w | ■ | |
| k | | | | | | w | w | | ■ |

s: strong, w: weak

## Computational Chemistry

### Methods

Molecular mechanics calculations on the complex ***t*-P12·(T6)$_2$** were performed using HyperChem 8. A modified form of HyperChem's MM+ forcefield was used, to which additional bond stretch, angle bend and torsion terms had been added to describe metalloporphyrins,[S4,S5] alkynes[S6] and butadiynes.[S7] Minimizations were performed using the steepest descent and Polak-Ribiere algorithms.

The optimized geometry and vibrational frequencies of ***t*-P12** were calculated at the restricted BLYP[S8-S10] level of theory employing the 6-31G(d) polarized valence-double-ξ basis set,[S11-S16] neglecting aryl sidegroups and templates using a C1 symmetry of ***t*-P12** within the calculation. Tight convergence criteria were used throughout. No imaginary frequencies were found for the optimized structure. Ground state vibrational frequencies of the butadiyne stretching vibrations are reported to draw a comparison to the HT active modes observed in the fluorescence spectra. All DFT calculations were carried out using Gaussian 09.[S17]

### Computed Cartesian coordinates and energies

***t*-P12** ($^1$A):

```
 BLYP/6-31G(d)  Energy= -35923.436575

C                  12.695507   -2.820423   -5.562617
C                  12.619954   -3.503908   -4.289524
C                  12.745310   -2.543715   -3.312988
C                  12.865190   -1.270188   -3.989612
N                  12.850587   -1.455452   -5.364608
H                  12.500438   -4.577889   -4.165112
H                  12.739365   -2.677958   -2.233706
C                  12.911405   -0.000727   -3.331708
C                  12.865336    1.268737   -3.989617
C                  12.745605    2.542280   -3.312999
N                  12.850753    1.453996   -5.364614
C                  12.620360    3.502484   -4.289539
H                  12.739677    2.676529   -2.233718
C                  12.695833    2.818985   -5.562629
H                  12.500969    4.576479   -4.165131
C                  12.628441    3.464541   -6.837820
C                  12.880982    2.818760   -8.091449
C                  12.990054    3.494593   -9.369190
N                  13.062316    1.459555   -8.249668
C                  13.255965    2.525381  -10.308978
H                  12.887789    4.567833   -9.515742
C                  13.277082    1.255884   -9.610954
H                  13.406801    2.652690  -11.380682
C                  13.407031   -0.000770  -10.221831
C                  13.276939   -1.257407   -9.610948
C                  13.255677   -2.526905  -10.308967
N                  13.062149   -1.461047   -8.249662
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H                  13.406499   -2.654236  -11.380670
C                  12.880658   -2.820231   -8.091437
H                  12.887266   -4.569310   -9.515722
C                  12.628041   -3.465977   -6.837805
Zn                 12.962418   -0.000737   -6.808174
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C                  11.693328   -5.944510   -6.873226
C                  12.222603    4.819989   -6.863915
C                  11.694015    5.943182   -6.873249
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C                   7.734283   10.816554   -9.605207
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| C | 12.865350 | 1.268743 | 3.989610 |

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| H | 12.500447 | -4.577882 | 4.165117 |
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| N | -12.850773 | -1.453994 | 5.364600 |
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| H | -12.739377 | 2.677962 | 2.233693 |
| C | -13.407067 | 0.000772 | 10.221815 |
| H | -13.406539 | 2.654238 | 11.380655 |
| C | -5.296782 | 11.664259 | 3.992533 |
| C | -3.874724 | 12.293193 | 5.570040 |
| C | -5.546676 | 12.056959 | 9.609770 |
| C | -3.983217 | 12.474967 | 8.096752 |
| C | -12.865352 | -1.268734 | 3.989604 |
| C | -12.695852 | -2.818982 | 5.562616 |
| C | -12.881009 | -2.818758 | 8.091435 |
| C | -13.277115 | -1.255882 | 9.610938 |
| C | -4.124339 | 12.180483 | 3.319459 |
| C | -3.233675 | 12.552510 | 4.299021 |
| C | -3.288973 | 12.565328 | 6.846872 |
| C | -4.436484 | 12.670090 | 10.310464 |
| C | -3.457088 | 12.912059 | 9.374815 |
| C | -12.745618 | -2.542277 | 3.312986 |
| C | -12.620375 | -3.502481 | 4.289526 |
| C | -12.628463 | -3.464538 | 6.837806 |
| C | -12.990084 | -3.494590 | 9.369175 |
| C | -13.255999 | -2.525379 | 10.308963 |
| H | -3.996922 | 12.231429 | 2.240526 |
| H | -2.239091 | 12.975935 | 4.178172 |
| C | -1.911176 | 12.886880 | 6.878335 |
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| H | -2.474193 | 13.354055 | 9.524227 |
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| H | -12.500982 | -4.576475 | 4.165119 |
| C | -12.222625 | -4.819985 | 6.863903 |
| H | -12.887819 | -4.567830 | 9.515728 |
| H | -13.406837 | -2.652688 | 11.380666 |
| C | -0.674350 | 12.991907 | 6.890255 |
| C | -11.694035 | -5.943178 | 6.873239 |
| C | -11.014635 | -7.109955 | 6.871983 |
| C | -10.298664 | -8.124000 | 6.860376 |
| C | -9.319889 | -9.145759 | 6.833258 |
| C | -8.890123 | -9.692510 | 8.085733 |
| C | -8.783623 | -9.513866 | 5.558817 |
| C | -9.538969 | -9.461440 | 9.361283 |
| N | -7.798246 | -10.521894 | 8.245167 |
| N | -7.671025 | -10.319984 | 5.362319 |
| C | -9.332927 | -9.102278 | 4.285037 |
| C | -8.832032 | -10.175946 | 10.300959 |

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| H | -10.422803 | -8.843758 | 9.506530 |
| C | -7.734290 | -10.816529 | 9.605213 |
| Zn | -6.469578 | -11.144949 | 6.807330 |
| C | -7.508558 | -10.414772 | 3.987632 |
| C | -8.553312 | -9.678188 | 3.309389 |
| H | -10.207539 | -8.467833 | 4.159747 |
| H | -9.022972 | -10.250420 | 11.371240 |
| C | -6.708446 | -11.552776 | 10.217436 |
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| C | -5.548062 | -12.056333 | 9.609794 |
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| C | -5.298107 | -11.663641 | 3.992559 |
| C | -4.437942 | -12.669593 | 10.310488 |
| C | -3.458571 | -12.911670 | 9.374842 |
| C | -3.290408 | -12.564948 | 6.846900 |
| C | -3.235102 | -12.552127 | 4.299050 |
| C | -4.125721 | -12.179996 | 3.319486 |
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| H | -2.475727 | -13.353778 | 9.524254 |
| C | -1.912647 | -12.886656 | 6.878366 |
| H | -2.240566 | -12.975665 | 4.178201 |
| H | -3.998307 | -12.230953 | 2.240553 |
| C | -0.675833 | -12.991820 | 6.890286 |
| C | 0.674341 | -12.991893 | 6.890287 |
| C | 1.911166 | -12.886859 | 6.878367 |
| C | 3.288963 | -12.565305 | 6.846904 |
| C | 3.983206 | -12.474942 | 8.096784 |
| C | 3.874715 | -12.293175 | 5.570072 |
| C | 3.457076 | -12.912029 | 9.374848 |
| N | 5.255662 | -11.962304 | 8.250680 |
| N | 5.137462 | -11.753761 | 5.367993 |
| C | 3.233666 | -12.552494 | 4.299054 |
| C | 4.436471 | -12.670060 | 10.310497 |
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| C | 5.546665 | -12.056932 | 9.609802 |
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| C | 5.296775 | -11.664248 | 3.992564 |
| C | 4.124331 | -12.180472 | 3.319490 |
| H | 2.239081 | -12.975918 | 4.178205 |
| H | 4.406688 | -12.870809 | 11.381164 |
| C | 6.707105 | -11.553507 | 10.217445 |
| N | 7.797032 | -10.522765 | 8.245173 |
| N | 7.669845 | -10.320859 | 5.362323 |
| C | 6.421146 | -11.076332 | 3.331957 |
| H | 3.996914 | -12.231421 | 2.240557 |
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| C | 8.889007 | -9.693508 | 8.085737 |
| C | 8.782535 | -9.514868 | 5.558820 |
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| C | 8.830851 | -10.176923 | 10.300966 |
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| C | 9.318839 | -9.146814 | 6.833259 |
| C | 9.331891 | -9.103351 | 4.285039 |
| C | 8.552212 | -9.679177 | 3.309392 |
| H | 9.021778 | -10.251412 | 11.371249 |
| H | 10.421779 | -8.844924 | 9.506534 |
| C | 10.297729 | -8.125165 | 6.860375 |
| H | 10.206576 | -8.469007 | 4.159747 |
| H | 8.659023 | -9.600448 | 2.229903 |
| C | 11.013808 | -7.111196 | 6.871981 |
| C | -6.428552 | -11.091417 | 1.915294 |
| C | -6.433019 | -11.101022 | 0.675762 |
| C | -6.428548 | -11.091425 | -1.915267 |
| C | -6.433018 | -11.101024 | -0.675735 |

| | | | |
|---|---|---|---|
| C | -12.936599 | 0.000724 | -1.915237 |
| C | -12.949965 | 0.000726 | -0.675744 |
| C | -12.936609 | 0.000728 | 1.915215 |
| C | -12.949969 | 0.000728 | 0.675721 |
| C | -6.427289 | 11.092166 | -1.915292 |
| C | -6.431759 | 11.101769 | -0.675760 |
| C | -6.427294 | 11.092166 | 1.915269 |
| C | -6.431760 | 11.101769 | 0.675737 |
| C | 6.428551 | 11.091420 | -1.915287 |
| C | 6.433019 | 11.101019 | -0.675755 |
| C | 6.428549 | 11.091413 | 1.915274 |
| C | 6.433018 | 11.101017 | 0.675742 |
| C | 12.936600 | -0.000725 | -1.915228 |
| C | 12.949965 | -0.000725 | -0.675735 |
| C | 12.936607 | -0.000723 | 1.915223 |
| C | 12.949968 | -0.000724 | 0.675730 |
| C | 6.427294 | -11.092169 | -1.915263 |
| C | 6.431760 | -11.101770 | -0.675730 |
| C | 6.427289 | -11.092162 | 1.915299 |
| C | 6.431758 | -11.101767 | 0.675766 |
| H | -6.790612 | 11.696701 | 11.298617 |
| H | 6.791955 | 11.695971 | -11.298629 |
| H | -6.790595 | 11.696703 | -11.298640 |
| H | -13.564570 | 0.000756 | -11.304245 |
| H | -6.791946 | -11.695991 | -11.298608 |
| H | 6.790607 | -11.696724 | -11.298609 |
| H | 13.564579 | -0.000781 | -11.304236 |
| H | 6.791948 | 11.695960 | 11.298617 |
| H | 13.564612 | -0.000762 | 11.304229 |
| H | 6.790601 | -11.696673 | 11.298648 |
| H | -6.791962 | -11.695940 | 11.298638 |
| H | -13.564618 | 0.000783 | 11.304220 |

**Herzberg-Teller vibration**

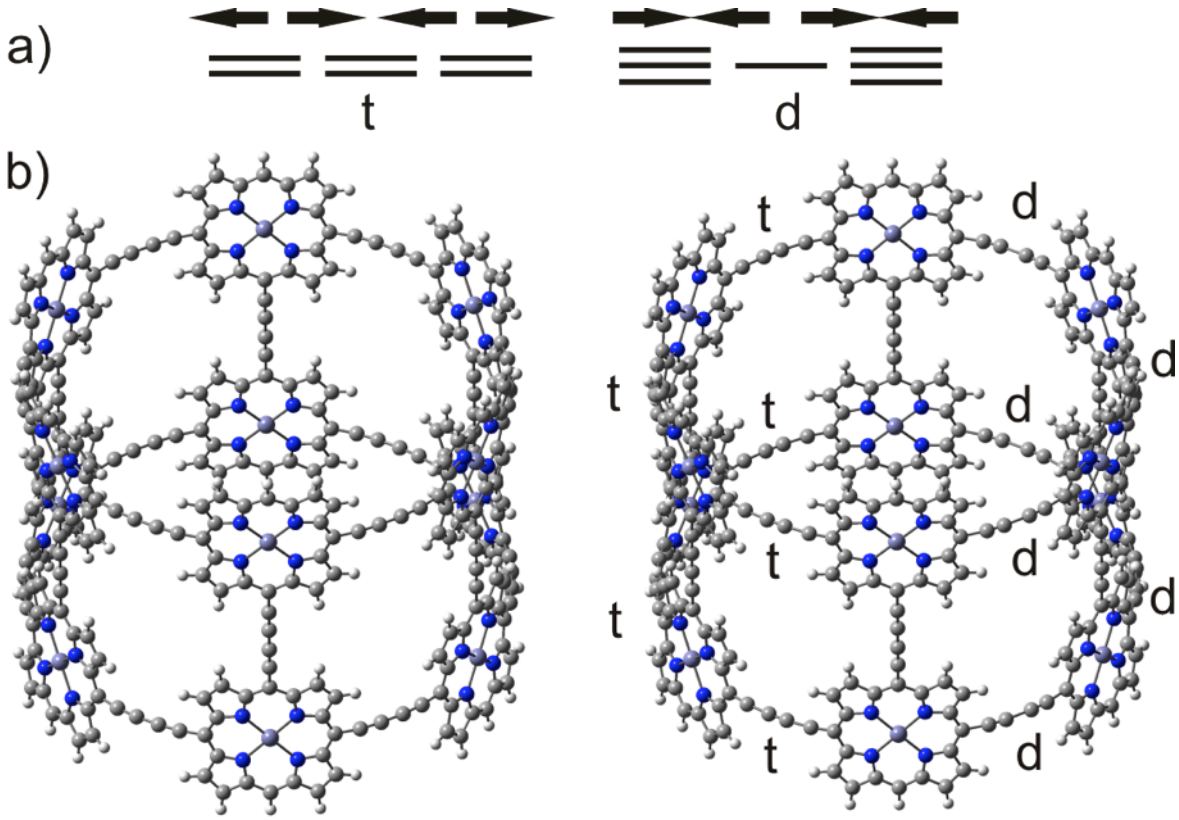


**Figure S3.** a) Direction of the change in bond length alternation during the butadiyne stretching vibration of ***t*-P12**, giving rise to a more hexatriene-like structure (labeled **t**, left side) or a butadiyne structure (labeled **d**, right side). b) Left side: Ground state structure of ***t*-P12**. Right side: Distortion (labels according to the description in a)) of the butadiyne bonds during the HT active vibration of **1**. The stretching vibration is calculated to be found at 2160 $cm^{-1}$ at the BLYP/6-31G(d) level of theory.

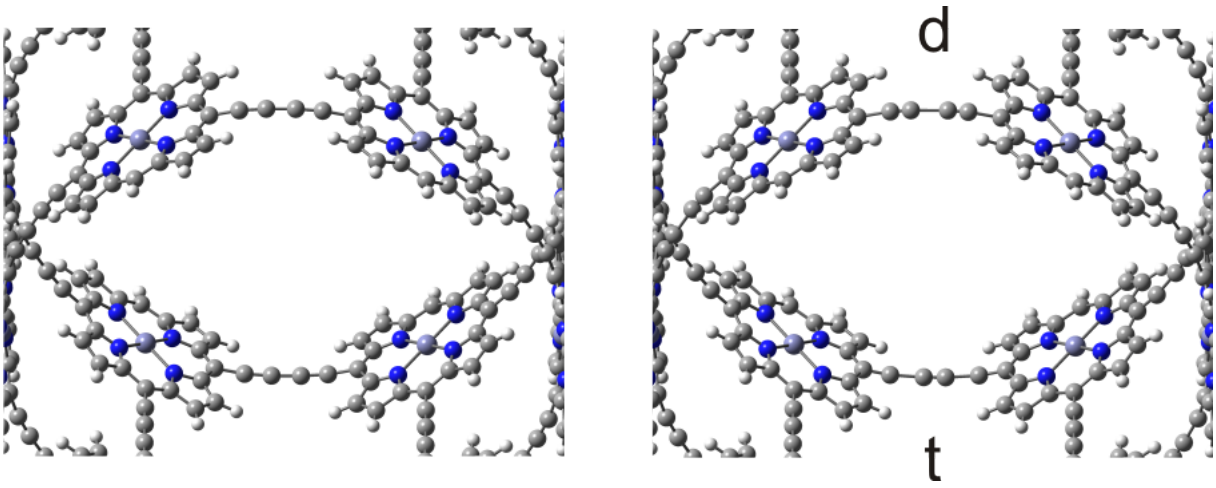


**Figure S4.** Left side: Ground state structure of ***t*-P12**. Right side: Zoom-in of the distortion (labels according to the description in Figure S3, only the distortions of two oppositely situated butadiynes of ***t*-P12** are shown for clarity, image is the same as on the left side) of the butadiyne bonds during a HT active vibration of ***t*-P12**. This stretching vibration is calculated to be found at 2160 $cm^{-1}$ at the BLYP/6-31G(d) level of theory.

## Photoluminescence Upconversion Spectroscopy

The photoluminescence (PL) upconversion technique was used to investigate fluorescence dynamics of sample solutions held in quartz cuvettes as described in detail elsewhere.[S18-S19]

An excitation pulse was generated by a mode-locked Ti:Sapphire laser with pulse duration of 100 fs and a repetition rate of 80 MHz. Fluorescence is collected and optically gated in a beta-barium-oxide (BBO) crystal by a vertically polarized time-delayed gate beam. The upconverted signal, which consists of sum-frequency photons from the gate pulse and the vertical component of the fluorescence, was collected, dispersed in a monochromator and detected using a nitrogen-cooled CCD. Using a combination of a half-wave plate and a Glan-Thompson polarizer, the polarization of the excitation pulse was varied and fluorescence intensity dynamics were recorded separately for components polarized parallel $I_{\parallel}$ and perpendicular $I_{\perp}$ to the excitation pulse polarization. The fluorescence anisotropy is defined using $\gamma = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$ and calculated from the measured components. The full-width-half-maximum of the instrumental response function was measured to be 270 fs. No anisotropy decay was observed, indicating that any polarization decay must occur within 200 fs for this level of signal-to-noise.

The concentration of the sample solution was on the order of $10^{-4}$ mol/L. The excitation fluence was kept low (0.32 μJ/cm$^2$) to avoid fluorescence quenching via exciton-exciton annihilation. The detection wavelength was 941 nm.

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