Supporting Information

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

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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 CaH₂. N-Bromosuccinimide was recrystallized from boiling water. 3,5-Trihexylsilylbromobenzene, hexakis-(4-phenylpyridine)benzene (T6) and 5,15-bis[(triisopropylsilyl)ethynyl]porphyrin (P1a) were synthesized according to literature procedures.

NMR spectra were recorded on a Bruker AVIII400, Bruker AVIII400 (400 MHz) or Bruker DRX500 (500 MHz) spectrometer. The residual solvent peak was used as internal reference (chloroform, ¹H δ = 7.26 ppm, ¹³C 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-triheksylsilylbromobenzene (0.65 g, 0.90 mmol) in Et₂O (5 mL) at -78 °C under N₂ 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 Et₃N (0.2 mL). The volatiles were removed in vacuo and the residue was taken up in CH₂Cl₂ (50 mL) and washed with H₂O (2 × 30 mL). The organic layer was dried over Na₂SO₄ and concentrated. Column chromatography (9:1 PE:CH₂Cl₂) afforded 1 (0.15 g, 0.11 mmol, 76%) as a purple solid. ¹H NMR (CDCl₃, 400 MHz): 10.06 (s, 1H), 7.95 (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). ¹³C NMR (CDCl₃, 125 MHz): 149.4 (4C α-pyrrrolyl), 146.4 (4C α-pyrrrolyl), 140.4 (2CH o-Ar), 140.2 (CH p-Ar), 139.7 (C ipso-Ar), 135.2 (2C m-Ar), 132.4 (2C β-pyrrrolyl), 131.7 (2C β-pyrrrolyl), 130.9 (2C β-pyrrrolyl), 123.7 (C meso), 108.6 (CH meso), 106.3 (2C meso), 100.8 (2C C=C), 99.5 (2C C=C), 33.7 (6CH₂ Si(CH₃)₃), 31.8 (6CH₂ Si(CH₃)₃), 24.3 (6CH₂ Si(CH₃)₃), 22.8 (6CH₂ Si(CH₃)₃), 19.2 (12CH₃ TIPS), 14.3 (6CH₁ Si(CH₃)₃), 12.9 (6CH₃ TIPS), 12.1 (6CH₂ Si(CH₃)₃).

MS (MALDI) calcd. for C₈₃H₁₃₄N₅Si₄Zn: 1310.97, found: 1311.16.

Zinc porphyrin 2
To a solution of 1 (0.15 g, 0.11 mmol) in CHCl₃ (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 CH₂Cl₂:pyridine). Compound 2 (1:1 complex with pyridine, 164 mg, 98%) was obtained as a purple solid. ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (2CH), 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 (3C), 33.7 (6CH₂), 31.8 (6CH₂), 24.2 (6CH₂), 22.8 (6CH₂), 19.3 (12CH₃), 14.3 (6CH₃), 12.9 (6CH), 12.1 (6CH₂). MS (MALDI) calcd. for C₈₃H₁₃₄N₅Si₄Zn: 1372.88, found: 1373.26.

Bromide-substituted porphyrin 3
To a solution of 2 (164 mg, 0.11 mmol) in CHCl₃ (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:CH₂Cl₂, Rf ≈ 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:CH₂Cl₂, + 1% pyridine) yielding 3 (97 mg, 0.067 mmol, 56%) as purple solid. ¹H NMR (CDCl₃, 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). ¹³C 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), 133.4 (2C), 133.1 (2C), 132.2 (2C), 131.3 (2C), 124.5 (C), 109.8 (106.0 (2C), 101.9 (2C), 98.2 (2C), 33.7 (6CH₂), 31.7 (6CH₂), 24.1 (6CH₂), 22.7 (6CH₂), 19.2 (12CH₃), 14.3 (6CH₃), 12.8 (6CH), 12.1 (6CH₂). MS (MALDI) calcd. for C₈₃H₁₃₄BrN₅Si₄Zn: 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), Pd₂dba₃ (6.4 mg, 0.007 mmol), Cul (1.3 mg, 0.007 mmol) and triphenylphosphine (3.7 mg, 0.014 mmol). Toluene (4 mL) and N,N-diospropylamine (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:CH₂Cl₂, + 1% pyridine) yielding 4 (98 mg, 0.067 mmol, 100%) as a purple solid. ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (6CH₂), 31.6 (6CH₂), 24.1 (6CH₂), 22.6 (6CH₂), 19.1

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(12CH₃), 14.2 (6CH₃), 12.7 (6CH), 12.0 (6CH₂), 0.5 (3CH₃). MS (MALDI) calcd. for C₉₆H₁₄₀N₆Si₃Zn: 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 K₂CO₃ (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 CH₂Cl₂ (30 mL) and washed with H₂O (2 × 30 mL). The organic layer was dried over Na₂SO₄ and concentrated. The residue was subjected to column chromatography (6:1 PE:CH₂Cl₂ +1% pyridine) yielding P1b (261 mg, 0.186 mmol, 98%) as a green-purple solid. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 (6CH₂), 31.7 (6CH₂), 24.2 (6CH₂), 22.8 (6CH₂), 21.9 (12CH₃), 14.3 (6CH₃), 12.8 (6CH), 12.1 (6CH₂). MS (MALDI) calcd. for C₉₆H₁₄₀N₆Si₃Zn: 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(PPh₃)₂Cl₃ (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:CH₂Cl₂ +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. ¹H NMR (CDCl₃, 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 C₁₇₂H₂₆₀N₆S₁₃Zn₃: 2796.75, found: 2794.58. UV/vis/NIR (chloroform) λ<sub>max</sub> (log ε): 459 (5.43), 482 (5.32), 514 (5.42), 664 (4.75), 705 (4.85).

Deprotected dimer P2 and t-P12-(T6)
To a solution of 5 (42 mg, 0.015 mmol) in CH₂Cl₂ (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 (CH₂Cl₂ +1% pyridine) yielding crude P2 (~35 mg) after evaporation. This was used in the next step without further purification. ¹H NMR (CDCl₃, 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), 1.55–1.43 (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 CHCl₃ (~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(PPh₃)₂Cl₃ (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 CH₂Cl₂. The material was further purified by size-exclusion chromatography (BioBeads SX-1, toluene) and finally subjected to recycling GPC yielding t-P12-(T6) (12 mg, 0.8 µmol, 32%) as a purple-pink solid. ¹H NMR (CDCl₃, 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, 174H). MS (MALDI-TOF) calculated for C₉₄₀H₁₄₄₀N₆₀₀Si₃₀Zn₁₂: 14994; found: 15036. UV/vis/NIR (toluene) λ<sub>max</sub> (log ε): 528 (5.89), 791 (5.60), 831 (5.72), 873 (5.71).
NMR Spectra

Compound 1

$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz
Compound 2

$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 100 MHz
Compound 3

$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz
Compound 4

$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 100 MHz
Compound P1b

$^1$H NMR, CDCl$_3$, 400 MHz

$^{13}$C NMR, CDCl$_3$, 400 MHz
Compound 5 and P2

\[ ^1H \text{NMR, CDCl}_3, 400 \text{ MHz} \]

\[ ^1H \text{NMR, CDCl}_3, 400 \text{ MHz} \]
$t$-P12·(T6)$_2$

$^1$H NMR, CDCl$_3$, 400 MHz

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   | s   | s   | w   |     |     |     |
| d | w   | s   | s   | w   | w   |     |     |     |     |
| g | w   | s   | w   | s   | w   | w   | w   |     |     |
| h | w   | s   | s   | s   | w   | w   | w   | w   |     |
| i | w   | w   | w   | s   | w   | w   | w   | w   | w   |
| j | w   | s   | w   |     |     |     |     |     |     |
| k | w   | w   |     |     |     |     |     |     |     |

s: strong, w: weak
Computational Chemistry

Methods
Molecular mechanics calculations on the complex \( t\text{-P12} \cdot (T6) \) 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, alkynes and butadiynes. Minimizations were performed using the steepest descent and Polak-Ribiere algorithms.

The optimized geometry and vibrational frequencies of \( t\text{-P12} \) were calculated at the restricted BLYP level of theory employing the 6-31G(d) polarized valence-double-\( \xi \) basis set, neglecting aryl sidegroups and templates using a C1 symmetry of \( t\text{-P12} \) 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.

Computed Cartesian coordinates and energies \( t\text{-P12} \) (\( 1\text{A} \)):

| 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 13.062031   | 1.459555 -8.249668 |
| C 13.255965   | 2.525361 -10.308978 |
| H 12.887789   | 4.567833 -9.515742 |
| H 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 |
| C 12.999654   | -3.496081 -9.369174 |
| 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 |
| C 12.222046   | -4.821377 -6.863895 |
| C 11.693328   | -5.944510 -6.873226 |
| C 12.222603   | 4.819989 -6.863915 |
| C 11.694015   | 5.943182 -6.873249 |
| C 6.708439    | 11.552804 -10.217428 |
| C 5.548056    | 12.056359 -9.609783 |
| C 7.734283    | 10.816554 -9.605207 |

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|   | N          | C          | H          | Zn         |   |
|---|------------|------------|------------|------------|---|
| N | -5.255661  | 11.962333  | -8.250669  |            |   |
| N | -5.137462  | 11.753781  | -5.367983  |            |   |
| H | -8.659015  | 9.600440   | -2.229903  |            |   |
| C | -6.421145  | 11.076339  | -3.331950  |            |   |
| C | -13.407023 | 0.000747   | -10.221840 |            |   |
| N | -13.062310 | -1.459573  | -8.249673  |            |   |
| N | -12.850749 | 2.654210   | -11.380686 |            |   |
| H | -12.406490 | 0.000722   | -3.331717  |            |   |
| C | -12.739365 | 2.677956   | -2.233722  |            |   |
| C | -5.546663  | 12.056964  | -9.609792  |            |   |
| C | -3.983207  | 12.474976  | -8.096772  |            |   |
| C | -5.296775  | 11.664263  | -3.992555  |            |   |
| C | -3.874717  | 12.293202  | -5.570059  |            |   |
| C | -13.277075 | -1.255905  | -9.610959  |            |   |
| C | -12.880976 | -2.818778  | -8.091450  |            |   |
| C | -12.695829 | -2.818996  | -5.562630  |            |   |
| C | -12.865333 | -1.268744  | -3.989622  |            |   |
| C | -4.436472  | 12.670099  | -10.310484 |            |   |
| C | -3.457078  | 12.912070  | -9.374834  |            |   |
| C | -3.288965  | 12.565338  | -6.846890  |            |   |
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| C | -12.990047 | -3.494613  | -9.369189  |            |   |
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| H | -12.887782 | -4.567854  | -9.515738  |            |   |
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| C | -8.553304  | -9.678199  | -3.309371  |            |   |
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| C | -4.125717  | -12.180013 | -3.319450  |            |   |
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| C |         | 0.674349  | -12.991930 | -6.890242 |
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| C |         | 9.318839  | -9.146836  | -6.833233 |
| C |         | 9.537874  | -9.462539  | -9.361261 |
| C |         | 8.830853  | -10.176964 | -10.300935 |
| H |         | 8.659026  | -9.600451  | -2.229874 |
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| C |         | 12.990083 | 3.494609   | 9.369178 |
| H |         | 13.406835 | 2.652710   | 11.380670 |
| C |         | 12.881006 | 2.818774   | 8.091439 |
| H |         | 12.887818 | 4.567849   | 9.515728 |
| C |         | 12.628462 | 3.464552   | 6.837809 |
| C |         | 12.695851 | 2.818994   | 5.562619 |
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| N |         | 12.850772 | 1.454005   | 5.364606 |
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| Atoms | X (Å) | Y (Å) | Z (Å) |
|-------|-------|-------|-------|
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| C     | 12.619965 | -3.503901 | 4.289527 |
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| C     | 12.628058 | -3.465965 | 6.837808 |
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| C     | 12.220595 | -4.821364 | 6.863902 |
| C     | 11.693338 | -5.944495 | 6.873238 |
| C     | 12.226222 | 4.819999 | 6.863903 |
| C     | 11.694030 | 5.943191 | 6.873236 |
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| H     | 8.660111 | 9.599443 | 2.229886 |
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| C     | 1.912638 | 12.886660 | 6.878336 |
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| C     | 3.458557 | 12.911680 | 9.374814 |
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| C     | 11.014630 | 7.109968 | 6.817977 |
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| H     | 10.422796 | 8.843780 | 9.506519 |
| H     | 9.022961 | 10.250444 | 11.371225 |
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| C       | 1.911166 | -12.886859 | 6.878367 |
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| C       | -6.428548 | -11.091425 | -1.915267 |
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| C   | -12.936599 | 0.000724 | 1.915237 |
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| 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 \textit{t-P12}, giving rise to a more hexatriene-like structure (labeled \textit{t}, left side) or a butadiyne structure (labeled \textit{d}, right side). b) Left side: Ground state structure of \textit{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 \textit{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 \textit{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 \textit{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.\(^{S18-819}\)

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 \(\mu\)J/cm\(^2\)) to avoid fluorescence quenching via exciton-exciton annihilation. The detection wavelength was 941 nm.

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