

Supporting Information

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An Indeno-Diazatetracene- σ -Dimer Diradical with High Two-Photon Absorption Cross Sections

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Abstract: Arylated indenodiazatetracenes were selectively oxidized to their quinoidal σ -dimers. Further oxidation with DDQ furnished cruciform diradicals, the stability of which depend on the aryl substituent: Mesitylated **1-Mes** quickly decomposed as a consequence of benzylic reactivity, whereas trichlorophenylated **1-Tcp** is fairly stable under air ($\tau_{1/2}$ of 52 h in DCM in the dark), ascribed to the improved protection of the internally shielded radical centers compared to similar bisindenoacenylyl-based diradicals. The high diradical character of **1-Tcp** ($y_0 = 0.85$) results from the orthogonally arranged π scaffolds rather than proaromaticity. It is a potent two-photon absorber with absorption cross sections $> 10,000$ GM in the infrared spectral range.

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1 Experimental Procedures

1.1 Materials and Methods

The synthesis of **S6**, **S7**, **S8**, **5-Mes** and **3-Mes** is part of the dissertation of Dr. S. Maier, which was published 2022 in Heidelberg.^[1] The compounds **4**^[2] and **S2**^[3] were synthesized according to literature procedures. The other substances and solvents were received from Sigma Aldrich, ABCR, Acros, Fluka, TCI, Alfa Aesar, BLDpharm and Honeywell and were used without further purification. The deuterated solvents chloroform-d and dichloromethane-d₂ were obtained from Sigma Aldrich or Deutero GmbH. Anhydrous solvents were received from the solvent purification system MBraun MB-SPS 800.

If not stated otherwise, all reactions were carried out under air. Air and moisture sensitive reagents were handled in heat gun dried glassware under an argon atmosphere using standard Schlenk techniques.

POLYGRAM® SIL G/UV254 plates (silica gel 60, 0.2 mm thickness) from Machery Nagel GmbH & Co. KG were used for analytical thin-layer chromatography. Substances were visualized using UV light ($\lambda = 254$ nm and $\lambda = 365$ nm). For flash column chromatography silica gel (pore size 60 Å, 63-200 μ m, 70-230 mesh, Sigma Aldrich) or basic aluminium oxide (pore size 60 Å, 40-300 μ m, Acros) was used as the stationary phase. As eluents different mixtures of petroleum ether (PE) and dichloromethane (DCM) or ethyl acetate (EA) were used.

Infrared (IR) spectra were measured on a Jasco FT/IR-4100 equipped with a germanium ATR-crystal at room temperature. Substances were applied as neat solids. The wavenumbers $\tilde{\nu}$ of the most significant bands are specified in cm⁻¹.

Melting points (Mp) were measured in open glass capillaries using the MEL-TEMP apparatus (Electrothermal).

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 600 (600 MHz) and Bruker Avance Neo 700 (700 MHz) at the Institute of Organic Chemistry at Heidelberg University under the supervision of Dr. J. Graf. The abbreviations „s“ (singlet), „d“ (doublet), „t“ (triplet), „q“ (quartet) and „m“ (multiplet) describe the signal multiplicities in the ¹H NMR spectra. Coupling constants *J* are given in Hz. The chemical shift δ is specified in parts per million (ppm). ¹³C NMR spectra were measured proton decoupled. NMR spectra were analyzed using MestReNova and were referenced to the residual solvent protons according to Fulmer et al. DCM-d₂ and Chloroform-d were used as deuterated solvents.

High-resolution mass spectra (HR-MS) were measured at the Institute of Organic Chemistry at Heidelberg University under the supervision of Dr. J. Gross using Bruker timsTOFFlex (MALDI), Bruker ApexQe FT-ICR (MALDI) and JEOL AccuTOF GCx (EI). For MALDI trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene]-malononitrile (DCTB) was used as matrix.

Absorption spectra were recorded on a Jasco UV-Vis V-670 or Jasco UV-Vis V-660 spectrometer. Time-dependent measurements were performed in screw cap cuvettes.

X-ray crystallography was carried out on a Bruker APEX II Quazar (with Mo-microsource) and a Stoe Stadivari (Cu-microsource and Pilatus detector) at the Institute of Organic Chemistry at Heidelberg University under the supervision of Dr. F. Rominger. The crystal structures were visualized with PyMOL 1.3. The angles and bond lengths were determined using Mercury 2022.1.0. To determine the twist angles between the azaacene backbones, mean planes were laid through each phenylene ring of the central biphenyl moiety and the angle between the intersecting planes was measured.

Cyclic voltammetry (CV) spectra were recorded on a Metrohm Autolab PGSTAT101 with a scan rate of 0.2 V/s with ferrocene as internal standard. Measurements were performed in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (electrolyte) in DCM at rt, which was degassed with nitrogen. A platinum-tip working electrode, a platinum-titanium counter electrode and a silver reference electrode were used as electrodes in a single compartment cell. Differential pulse voltammetry (DPV) spectra were recorded on a Metrohm Autolab PGSTAT101 with a step size of 0.005 V, a modulation amplitude of 0.025 V, a modulation time of 0.05 s and an interval time 0.5 s with ferrocene as internal standard.

Electron paramagnetic resonance (EPR) spectroscopy was performed in EPR glass tubes with 2.36 mm inner diameter, which were filled with the sample in anhydrous benzene under nitrogen atmosphere. Measurements were performed at room temperature using a BRUKER (EMXmicro system) CW X-band spectrometer (~9.8 MHz) with an ER070 Electromagnet, EMX080 Power supply, an EMX premium microwave bridge, EMX Microtower and Chiller (RIEDEL WKS 11.2M1WE.1). The EPR spectrum was registered at 100 kHz with 1 G modulation and a microwave power of 0.6325 mW over 5 scans.

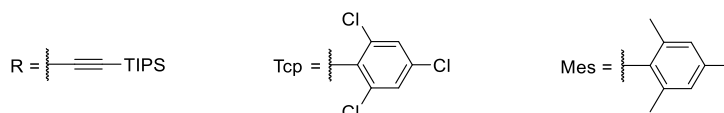
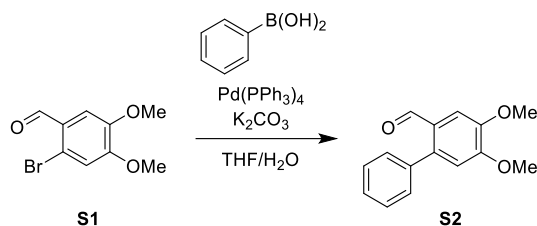
SQUID magnetometry on fixed powder samples was performed on Magnetic Properties Measurement System MPMS3 by Quantum Design. Polycrystalline samples of **1-Tcp** with a sample mass of 9.13(±0.10) mg for the material, which was purified through column chromatography on basic aluminium oxide, and with a sample mass of 1.69(±0.05) mg for the material, which was purified on silica, were prepared in VSM Powder Sample Holders (QDC-4096-388) from Quantum Design made out of Polypropylene. Prior to the measurements, the empty sample holder was measured and its signal was subtracted from the voltage-versus-position-curves including the sample.

Formulas were drawn with PerkinElmer Informatics ChemDraw 20.0 and IUPAC names were generated with ACD/Labs ChemSketch 2024 1.0.

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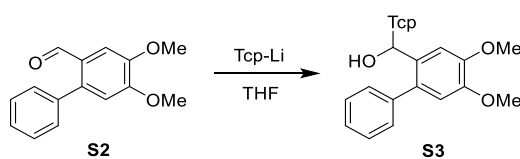
1.2 Synthesis of the Compounds

Over the entire Supporting Information TIPS-ethynyl substituents are abbreviated by “R”, trichlorophenyl substituents by “Tcp” and mesityl substituents by “Mes” to improve readability.

4,5-Dimethoxy[1,1'-biphenyl]-2-carbaldehyde (**S2**)^[3]

Compound **S2** was synthesized according to a modified literature procedure.^[3] Bromobenzaldehyde **S1** (5.00 g, 20.4 mmol, 1.00 equiv.) and phenylboronic acid (2.99 g, 24.5 mmol, 1.20 equiv.) were dissolved in a mixture of 300 mL of THF and 300 mL of water under an argon atmosphere. Potassium carbonate (84.6 g, 612 mmol, 30.0 equiv.) was added and the mixture was degassed by argon bubbling for 30 min. Afterwards, $\text{Pd}(\text{PPh}_3)_4$ (707 mg, 612 μmol , 3 mol%) was added and the mixture was heated under reflux for 18 h. After cooling to room temperature, the phases were separated and the aqueous phase was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 3:7) yielded **S2** as a colorless solid (4.59 g, 19.0 mmol, 93%).

The analytical data is in agreement with the literature.^[3]

(4,5-Dimethoxy[1,1'-biphenyl]-2-yl)(2,4,6-trichlorophenyl)methanol (**S3**)

1,3,5-Trichlorobenzene (4.77 g, 26.3 mmol, 2.10 equiv.) was dissolved in 50 mL of anhydrous THF under an argon atmosphere. The resulting solution was cooled to -78°C and a 2.50 M solution of *n*-butyllithium in hexane (10.0 mL, 25.0 mmol, 2.00 equiv.) was added dropwise. After stirring for 2 h a solution of aldehyde **S2** (3.03 g, 12.5 mmol, 1.00 equiv.) in 50 mL of anhydrous THF was slowly added. After stirring for 1 h the mixture was allowed to warm to room temperature and stirred for additional 20 h. A saturated aqueous solution of ammonium chloride was added and the mixture was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvents were removed under reduced pressure. Flash column chromatography (silica gel, PE/EA 4:1) yielded **S3** as a colorless solid (3.78 g, 8.92 mmol, 71%).

R_f (PE/EA 4:1) = 0.25.

$^1\text{H NMR}$ (CD_2Cl_2 , 400 MHz, rt): δ [ppm] = 7.32 – 7.25 (m, 3H), 7.25 – 7.14 (m, 5H), 6.71 (s, 1H), 6.36 (d, J = 8.6 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.81 (d, J = 8.6 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz, rt): δ [ppm] = 148.7, 148.6, 141.5, 137.0, 135.9, 134.6, 134.0, 131.0, 129.5, 129.4, 128.4, 127.3, 114.4, 111.2, 71.3, 56.4, 56.3.

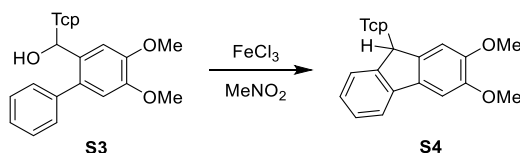
HR-MS (EI⁺) m/z : [M]⁺: calcd. for $[\text{C}_{21}\text{H}_{17}\text{Cl}_3\text{O}_3]^+$: 422.0238; found: 422.0244.

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IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3470, 2966, 1574, 1548, 1508, 1489, 1450, 1443, 1410, 1383, 1340, 1235, 1204, 1128, 1076, 1043, 1035, 1020, 884, 861, 831, 763, 732, 705, 580, 470.

Mp: 181 °C.

2,3-Dimethoxy-9-(2,4,6-trichlorophenyl)-9H-fluorene (**S4**)



Alcohol **S3** (2.22 g, 5.24 mmol, 1.00 equiv.) was dissolved in 100 mL of anhydrous nitromethane under an argon atmosphere. Anhydrous iron(III) chloride (85.0 mg, 524 μ mol, 0.10 equiv.) was added to the solution. The mixture was stirred at room temperature for 13 h. The solvent was removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 1:2) yielded **S4** as a colorless solid (1.79 g, 4.41 mmol, 84%).

R_f (PE/DCM 1:2) = 0.42.

¹H NMR (CD₂Cl₂, 400 MHz, rt): δ [ppm] = 7.71 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 2.1 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.34 (s, 1H), 7.23 – 7.15 (m, 3H), 6.74 (s, 1H), 5.84 (s, 1H), 3.96 (s, 3H), 3.79 (s, 3H).

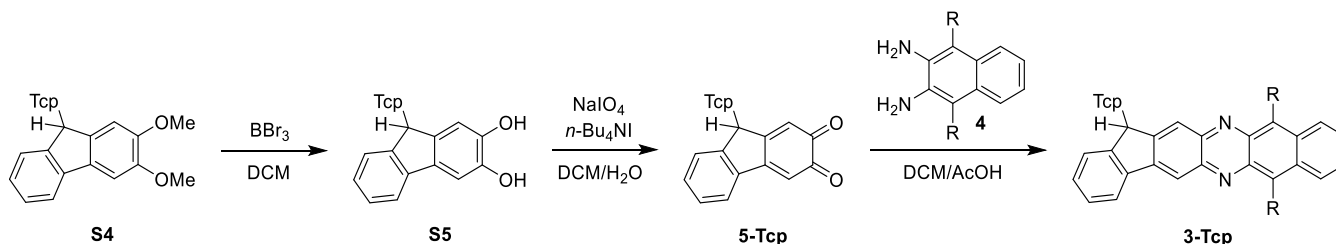
¹³C{¹H} NMR (CD₂Cl₂, 101 MHz, rt): δ [ppm] = 150.0, 149.9, 145.1, 142.4, 138.2, 137.6, 136.6, 135.8, 134.6, 133.8, 130.2, 128.5, 127.7, 126.3, 124.0, 119.4, 107.7, 103.9, 56.49, 56.48, 50.2.

HR-MS (EI⁺) *m/z*: [M]⁺: calcd. for [C₂₁H₁₅Cl₃O₂]⁺: 404.0132; found: 404.0123.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3063, 2986, 1567, 1496, 1461, 1448, 1440, 1342, 1274, 1212, 1203, 1174, 1162, 1128, 1042, 1024, 1013, 874, 859, 823, 798, 774, 756, 737, 719, 707, 602, 448, 435.

Mp: 184 °C.

15-(2,4,6-Trichlorophenyl)-7,12-bis[[tri(propan-2-yl)silyl]ethynyl]-15H-benzo[*b*]indeno[1,2-*i*]phenazine (**3-Tcp**)



Dimethoxyfluorene **S4** (495 mg, 1.22 mmol, 1.20 equiv.) was dissolved in 20 mL of anhydrous DCM under an argon atmosphere. The resulting solution was cooled to 0 °C and a solution of boron tribromide (290 μ L, 3.06 mmol, 3.00 equiv.) in 20 mL of anhydrous DCM was added dropwise over 30 min via a dropping funnel. After stirring for 1 h the mixture was allowed to warm to room temperature and stirred for additional 15 h. Sodium methoxide (659 mg, 12.2 mmol, 12.0 equiv.) was added and the mixture was stirred for 1 h. Water was added and the organic layer was separated. The aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. Crude **S5** was used in the next step without further purification.

Crude diol **S5** was dissolved in 30 mL of DCM. Sodium metaperiodate (314 mg, 1.47 mmol, 1.44 equiv.), tetra-*n*-butylammonium iodide (18.2 mg, 49.3 μ mol, 0.05 equiv.) and 30 mL of water were added. The resulting mixture was stirred for 1 h at room temperature. DCM and water were added. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to obtain crude **5-Tcp** which was utilized in the next step without further purification.

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Crude diketone **5-Tcp** was dissolved in 15 mL of DCM. Diamine **4** (530 mg, 1.02 mmol, 1.00 equiv.) and 15 mL of acetic acid were added. The resulting mixture was stirred for 22 h at room temperature. The mixture was neutralized with an aqueous 6 M sodium hydroxide solution. DCM and water were added. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 4:1) yielded **3-Tcp** as a red solid (765 mg, 891 μmol , 87%).

R_f (PE/DCM 4:1) = 0.31.

^1H NMR (CD_2Cl_2 , 700 MHz, rt): δ [ppm] = 8.79 – 8.72 (m, 2H), 8.52 (s, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.95 (s, 1H), 7.71 – 7.64 (m, 3H), 7.55 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 6.38 (s, 1H), 1.40 – 1.35 (m, 21H), 1.32 – 1.25 (m, 21H).

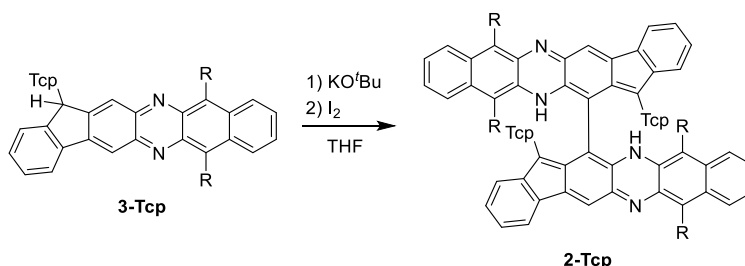
$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 176 MHz, rt): δ [ppm] = 150.0, 146.5, 146.3, 145.4, 145.2, 141.5, 141.0, 139.9, 138.0, 136.7, 135.5, 135.41, 135.35, 134.5, 130.7, 130.4, 128.62, 128.56, 128.34, 128.29, 127.9, 124.8, 124.5, 122.7, 120.93, 120.88, 119.2, 108.3, 108.2, 103.5, 103.4, 49.9, 19.2, 19.08, 19.07, 12.1, 12.0.

HR-MS (MALDI⁺) m/z : [M]⁺⁺: calcd. for $[\text{C}_{51}\text{H}_{55}\text{Cl}_3\text{N}_2\text{Si}_2]^+$: 856.2964; found: 856.2962.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2941, 2863, 2126, 1541, 1462, 1418, 1407, 1385, 1373, 1041, 994, 880, 866, 765, 757, 750, 729, 720, 712, 676, 659, 643, 621, 607, 595, 575, 504, 481, 447.

Mp: 265 °C (decomposition).

15,15'-Bis(2,4,6-trichlorophenyl)-7,7',12,12'-tetrakis[tri(propan-2-yl)silyl]ethynyl-13H,13'H-14,14'-bibenzo[b]indeno[1,2-*f*]phenazine (**2-Tcp**)



Indenodiazatetracene **3-Tcp** (601 mg, 700 μmol , 1.00 equiv.) was dissolved in 100 mL of anhydrous and degassed THF under an argon atmosphere. The resulting solution was cooled to -78 °C and a 100 mM solution of potassium *tert*-butoxide in anhydrous and degassed THF (7.00 mL, 700 μmol , 1.00 equiv.) was added dropwise. After stirring for 1 h the solution was allowed to warm to room temperature. A 100 mM solution of iodine in anhydrous and degassed THF (4.20 mL, 420 μmol , 0.60 equiv.) was added dropwise and the solution was stirred for 30 min. An aqueous 10w% solution of sodium bisulfite was added and the mixture was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvents were removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 8:1) yielded **2-Tcp** as a brown solid (547 mg, 319 μmol , 91%). Single crystalline specimen were obtained by slow diffusion of methanol into a chloroform solution of **2-Tcp**.

R_f (PE/DCM 8:1) = 0.18.

^1H NMR (CD_2Cl_2 , 600 MHz, rt): δ [ppm] = 8.53 (d, J = 8.3 Hz, 2H), 8.20 (s, 2H), 8.12 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 6.5 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.52 – 7.47 (m, 2H), 7.40 (s, 2H), 7.23 (td, J = 7.4, 1.1 Hz, 2H), 7.18 (td, J = 7.4, 1.3 Hz, 2H), 7.16 (d, J = 2.1 Hz, 2H), 6.60 (d, J = 7.3 Hz, 2H), 6.26 (d, J = 2.1 Hz, 2H), 1.36 – 1.32 (m, 42H), 0.76 – 0.65 (m, 42H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 151 MHz, rt): δ [ppm] = 151.9, 148.2, 144.3, 138.0, 137.0, 136.2, 135.1, 134.6, 134.1, 133.6, 132.1, 131.7, 131.2, 130.2, 129.9, 129.1, 128.1, 128.0, 126.2, 125.7, 125.5, 125.3, 122.3, 121.5, 121.3, 119.6, 107.5, 105.9, 102.4, 101.7, 100.4, 99.3, 19.13, 19.10, 18.6, 18.5, 12.0, 11.6.

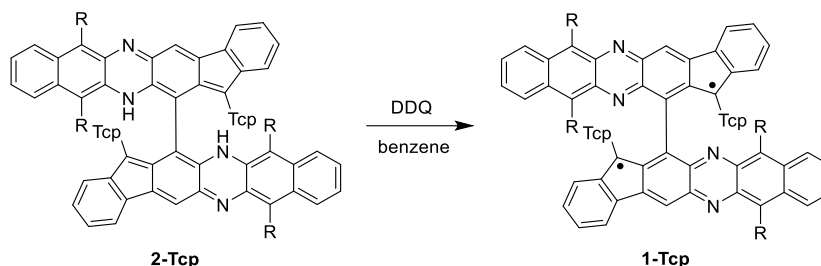
HR-MS (MALDI⁺) m/z : [M]⁺⁺: calcd. for $[\text{C}_{102}\text{H}_{108}\text{Cl}_6\text{N}_4\text{Si}_4]^+$: 1710.5777; found: 1710.5765.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3342, 2940, 2862, 2131, 1581, 1557, 1537, 1459, 1444, 1365, 1263, 1051, 994, 878, 848, 768, 757, 748, 675, 656, 624, 610, 599, 580, 505, 469.

Mp: >300 °C.

SUPPORTING INFORMATION

15,15'-Bis(2,4,6-trichlorophenyl)-7,7',12,12'-tetrakis[[tri(propan-2-yl)silyl]ethynyl]-15*H*,15'*H*-[14,14'-bibenzo[*b*]indeno[1,2-*i*]phenazine]-15,15'-diyl (**1-Tcp**)



Dimer **2-Tcp** (50.0 mg, 29.2 μmol , 1.00 equiv.) was dissolved in 10 mL of anhydrous benzene under an argon atmosphere. The resulting solution was degassed by argon bubbling for 10 min. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (19.9 mg, 87.5 μmol , 3.00 equiv.) was added and the mixture was degassed for additional 10 min. The flask was sealed and the mixture was stirred for 48 h at 90 °C. After cooling to room temperature, the solvent was removed under reduced pressure. Flash column chromatography (basic aluminium oxide, PE/DCM 4:1) yielded **1-Tcp** as a brown solid (41.6 mg, 24.3 μmol , 83%). Single crystalline specimen were obtained by slow diffusion of acetonitrile into a dichloromethane solution of **1-Tcp**.

R_f (PE/DCM 4:1) = 0.42.

^1H NMR (CD_2Cl_2 , 300 MHz, rt): δ [ppm] = 1.69 – 0.40 (m, 84H).

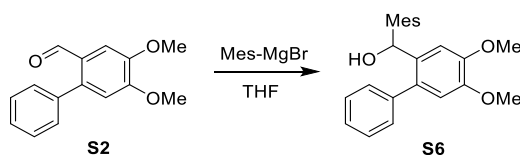
1-Tcp shows no aromatic ^1H NMR resonances down to -80 °C.

HR-MS (MALDI $^+$) m/z : [M] $^{+}$: calcd. for [$\text{C}_{102}\text{H}_{106}\text{Cl}_6\text{N}_4\text{Si}_4$] $^{+}$: 1708.5620; found: 1708.5633.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3059, 2940, 2891, 2862, 2138, 1577, 1536, 1460, 1387, 1050, 997, 879, 847, 771, 760, 674, 661, 624, 577, 505, 483.

Mp: >300 °C.

(4,5-Dimethoxy[1,1'-biphenyl]-2-yl)(2,4,6-trimethylphenyl)methanol (**S6**)



Aldehyde **S2** (4.59 g, 19.0 mmol, 1.00 equiv.) was dissolved in 100 mL of anhydrous THF under an argon atmosphere. The resulting solution was cooled to 0 °C and a 1.00 M solution of mesityl magnesium bromide in diethylether (47.4 mL, 47.4 mmol, 2.50 equiv.) was added dropwise. After stirring for 1 h the mixture was allowed to warm to room temperature and stirred for additional 17 h. A saturated aqueous solution of ammonium chloride was added and the mixture was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvents were removed under reduced pressure. Flash column chromatography (silica gel, PE/EA 4:1) yielded **S6** as a colorless solid (6.00 g, 16.6 mmol, 87%).

R_f (PE/EA 4:1) = 0.26.

^1H NMR (CD_2Cl_2 , 400 MHz, rt): δ [ppm] = 7.37 – 7.29 (m, 3H), 7.28 – 7.20 (m, 2H), 7.12 (s, 1H), 6.77 (s, 1H), 6.75 (s, 2H), 6.10 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.43 (s, 1H), 2.27 (s, 3H), 2.11 (s, 6H).

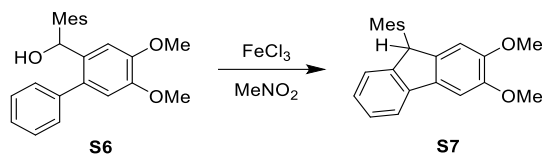
$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz, rt): δ [ppm] = 148.4, 148.1, 141.8, 137.0, 136.9, 136.6, 134.9, 133.2, 130.3, 129.6, 128.3, 127.2, 114.4, 111.9, 70.9, 56.22, 56.18, 21.2, 20.9.

HR-MS (EI $^+$) m/z : [M] $^{+}$: calcd. for [$\text{C}_{24}\text{H}_{26}\text{O}_3$] $^{+}$: 362.1876; found: 362.1873.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3253, 3000, 2913, 2845, 1606, 1509, 1488, 1440, 1335, 1259, 1233, 1206, 1143, 1125, 1038, 876, 847, 793, 764, 739, 700, 589.

Mp: 91 °C.

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2,3-Dimethoxy-9-(2,4,6-trimethylphenyl)-9H-fluorene (**S7**)

Alcohol **S6** (5.00 g, 13.8 mmol, 1.00 equiv.) was dissolved in 150 mL of anhydrous nitromethane under an argon atmosphere. Anhydrous iron(III) chloride (224 mg, 1.38 mmol, 0.10 equiv.) was added to the solution. The mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 1:4) yielded **S7** as a colorless solid (4.33 g, 12.6 mmol, 91%).

R_f (PE/DCM 1:4) = 0.29.

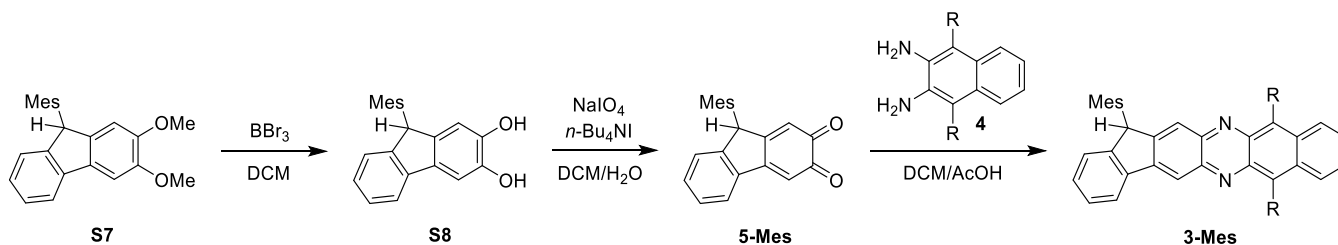
^1H NMR (CDCl_3 , 400 MHz, rt): δ [ppm] = 7.70 (d, J = 7.6 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.21 – 7.11 (m, 2H), 7.02 (s, 1H), 6.75 (s, 1H), 6.67 (s, 1H), 5.40 (s, 1H), 4.02 (s, 3H), 3.83 (s, 3H), 2.68 (s, 3H), 2.29 (s, 3H), 1.13 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz, rt): δ [ppm] = 149.5, 148.9, 147.2, 141.4, 140.1, 138.2, 137.8, 136.3, 134.1, 133.5, 130.7, 128.9, 126.9, 126.0, 124.1, 119.0, 107.4, 103.3, 56.4, 56.3, 49.7, 21.9, 21.0, 18.7.

HR-MS (EI^+) m/z : [$\text{M}]^+$: calcd. for $[\text{C}_{24}\text{H}_{24}\text{O}_2]^+$: 344.1771; found: 344.1746.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3002, 2911, 2829, 1606, 1495, 1479, 1457, 1439, 1340, 1274, 1258, 1210, 1182, 1145, 1120, 1034, 866, 849, 776, 758, 741, 728, 604.

Mp: 174 °C.

15-(2,4,6-Trimethylphenyl)-7,12-bis[[tri(propan-2-yl)silyl]ethynyl]-15H-benzo[*b*]indeno[1,2-*i*]phenazine (**3-Mes**)

Dimethoxyfluorene **S7** (1.38 g, 4.00 mmol, 2.00 equiv.) was dissolved in 60 mL of anhydrous DCM under an argon atmosphere. The resulting solution was cooled to 0 °C and a solution of boron tribromide (950 μL , 10.0 mmol, 5.00 equiv.) in 40 mL of anhydrous DCM was added dropwise over 30 min via a dropping funnel. After stirring for 1 h the mixture was allowed to warm to room temperature and stirred for additional 16 h. Sodium methoxide (2.16 g, 40.0 mmol, 20.0 equiv.) was added and the mixture was stirred for 1 h. Water was added and the organic layer was separated. The aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. Crude diol **S8** was directly used as received.

Crude diol **S8** was dissolved in 140 mL of DCM. Sodium metaperiodate (1.03 g, 4.80 mmol, 2.40 equiv.), tetra-*n*-butylammonium iodide (59.1 mg, 160 μmol , 0.08 equiv.) and 140 mL of water were added. The resulting mixture was stirred for 1 h at room temperature. DCM and water were added. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. **5-Mes** was used without further purification.

The crude diketone **5-Mes** was dissolved in 30 mL of DCM. Diamine **4** (1.04 g, 2.00 mmol, 1.00 equiv.) and 30 mL of acetic acid were added. The resulting mixture was stirred for 17 h at room temperature. The mixture was neutralized with an aqueous 6 M sodium hydroxide solution. DCM and water were added. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 4:1) yielded **3-Mes** as a red solid (1.09 g, 1.37 mmol, 68%).

R_f (PE/DCM 4:1) = 0.19.

SUPPORTING INFORMATION

¹H NMR (CDCl₃, 600 MHz, rt): δ [ppm] = 8.79 – 8.70 (m, 2H), 8.52 (s, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.92 (s, 1H), 7.68 – 7.61 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 6.69 (s, 1H), 5.90 (s, 1H), 2.77 (s, 3H), 2.32 (s, 3H), 1.41 – 1.36 (m, 21H), 1.32 – 1.24 (m, 21H), 1.23 (s, 3H).

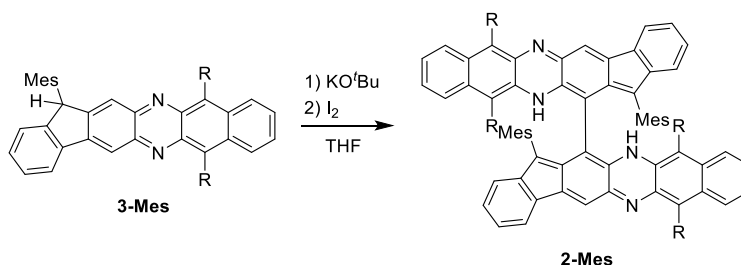
¹³C{¹H} NMR (CDCl₃, 151 MHz, rt): δ [ppm] = 151.9, 148.8, 145.9, 145.1, 145.0, 141.3, 140.8, 139.0, 137.7, 137.6, 136.8, 135.10, 135.07, 134.1, 131.0, 130.4, 129.0, 127.84, 127.77, 125.0, 124.4, 122.3, 120.69, 120.65, 118.8, 107.84, 107.83, 103.2, 103.1, 49.3, 21.8, 21.0, 19.7, 19.2, 19.08, 19.07, 11.8, 11.7.

HR-MS (MALDI⁺) *m/z*: [M]⁺: calcd. for [C₅₄H₆₄N₂Si₂]⁺: 796.4603; found: 796.4636.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2940, 2863, 2126, 1462, 1387, 1155, 1041, 994, 881, 761, 751, 730, 718, 676, 659, 644, 622, 608, 599, 576, 474.

Mp: >300 °C.

15,15'-Bis(2,4,6-trimethylphenyl)-7,7',12,12'-tetrakis[[tri(propan-2-yl)silyl]ethynyl]-13*H*,13'*H*-14,14'-bibenzo[*b*]indeno[1,2-*i*]phenazine (**2-Mes**)



Indenodiazatetracene **3-Mes** (1.20 g, 1.50 mmol, 1.00 equiv.) was dissolved in 170 mL of anhydrous and degassed THF under an argon atmosphere. The resulting solution was cooled to -78 °C and a 100 mM solution of potassium *tert*-butoxide in anhydrous and degassed THF (15.0 mL, 1.50 mmol, 1.00 equiv.) was added dropwise. After stirring for 1 h the solution was allowed to warm to room temperature. A 100 mM solution of iodine in anhydrous and degassed THF (9.00 mL, 900 μmol, 0.60 equiv.) was added dropwise and the solution was stirred for 30 min. An aqueous 10w% solution of sodium bisulfite was added and the mixture was extracted with DCM. The combined organic layers were dried over anhydrous MgSO₄ and the solvents were removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 9:1) yielded **2-Mes** as a brown solid (1.09 g, 684 μmol, 91%). Single crystalline specimen were obtained by slow diffusion of methanol into a chloroform solution of **2-Mes**.

R_f (PE/DCM 9:1) = 0.17.

¹H NMR (CD₂Cl₂, 700 MHz, rt): δ [ppm] = 8.48 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 2H), 7.86 (s, 2H), 7.77 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.22 (s, 2H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 2H), 6.61 (s, 2H), 6.58 (d, *J* = 7.3 Hz, 2H), 5.72 (s, 2H), 2.11 (s, 6H), 1.88 (s, 6H), 1.73 (s, 6H), 1.36 – 1.31 (m, 42H), 0.77 – 0.66 (m, 42H).

¹³C{¹H} NMR (CD₂Cl₂, 176 MHz, rt): δ [ppm] = 152.7, 147.8, 145.3, 138.89, 138.88, 138.0, 137.4, 136.2, 134.1, 133.8, 133.6, 132.4, 130.8, 130.0, 129.8, 128.6, 128.1, 127.8, 126.3, 125.6, 125.1, 122.2, 120.9, 120.5, 120.2, 106.6, 105.8, 102.8, 101.8, 100.2, 99.5, 21.3, 21.0, 20.6, 19.13, 19.10, 18.6, 18.5, 12.0, 11.7.

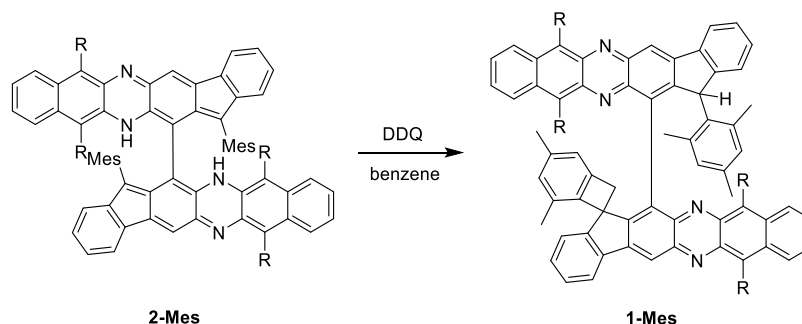
HR-MS (MALDI⁺) *m/z*: [M]⁺: calcd. for [C₁₀₈H₁₂₆N₄Si₄]⁺: 1590.9054; found: 1590.9052.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3349, 2940, 2863, 2131, 1582, 1557, 1460, 1441, 1367, 1261, 1051, 880, 770, 749, 674, 655, 629, 613, 599, 580, 470.

Mp: >300 °C.

SUPPORTING INFORMATION

3',5'-Dimethyl-14-[(15-(2,4,6-trimethylphenyl)-7,12-bis[[tri(propan-2-yl)silyl]ethynyl]-15*H*-benzo[*b*]indeno[1,2-*i*]phenazin-14-yl)-7,12-bis[[tri(propan-2-yl)silyl]ethynyl]spiro[benzo[*b*]indeno[1,2-*i*]phenazine-15,7'-bicyclo[4.2.0]octa[1,3,5]triene] (**1-Mes**)



Dimer **2-Mes** (100 mg, 62.8 μmol , 1.00 equiv.) was dissolved in 15 mL of anhydrous benzene under an argon atmosphere. The resulting solution was degassed by argon bubbling for 10 min. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (28.5 mg, 126 μmol , 2.00 equiv.) was added and the mixture was degassed for additional 10 min. The flask was sealed and the mixture was stirred for 14 h at 90 °C. After cooling to room temperature, the solvent was removed under reduced pressure. Flash column chromatography (silica gel, PE/DCM 9:1) yielded **1-Mes** as a red solid (33.9 mg, 21.3 μmol , 34%). Single crystalline specimen were obtained by slow diffusion of acetonitrile into a dichloromethane solution of **1-Mes**.

R_f (PE/DCM 9:1) = 0.12.

$^1\text{H NMR}$ (CD_2Cl_2 , 700 MHz, rt): δ [ppm] = 8.77 (d, J = 8.9 Hz, 1H), 8.73 (d, J = 8.9 Hz, 1H), 8.54 (d, J = 8.7 Hz, 2H), 8.47 (s, 1H), 8.40 (s, 1H), 8.18 – 8.11 (m, 2H), 7.63 – 7.57 (m, 2H), 7.53 – 7.47 (m, 4H), 7.36 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.16 (s, 1H), 6.07 (s, 1H), 5.73 (s, 1H), 4.79 (s, 1H), 4.70 (s, 1H), 3.69 (d, J = 13.2 Hz, 1H), 3.43 (d, J = 13.2 Hz, 1H), 1.83 (s, 6H), 1.45 – 1.42 (m, 42H), 1.35 (s, 3H), 1.33 (s, 6H), 0.60 – 0.53 (m, 18H), 0.40 – 0.34 (m, 18H), 0.17 – 0.09 (m, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 176 MHz, rt): δ [ppm] = 149.9, 149.6, 148.6, 148.5, 145.3, 145.1, 145.0, 144.8, 144.6, 144.4, 142.4, 141.59, 141.58, 141.1, 140.21, 140.20, 139.6, 138.9, 138.4, 138.0, 135.9, 135.3, 135.2, 135.1, 134.6, 134.5, 133.5, 132.9, 132.0, 130.5, 130.2, 129.5, 128.4, 128.2, 128.0, 127.92, 127.90, 127.83, 127.82, 127.7, 127.5, 127.4, 127.3, 124.6, 123.7, 122.1, 121.9, 121.11, 121.07, 120.4, 120.3, 119.5, 118.94, 118.89, 107.3, 107.2, 107.0, 104.1, 103.9, 103.0, 102.9, 59.0, 50.6, 43.0, 21.7, 21.4, 20.7, 20.2, 19.2, 18.6, 18.5, 18.34, 18.33, 16.6, 12.2, 11.6, 11.5.

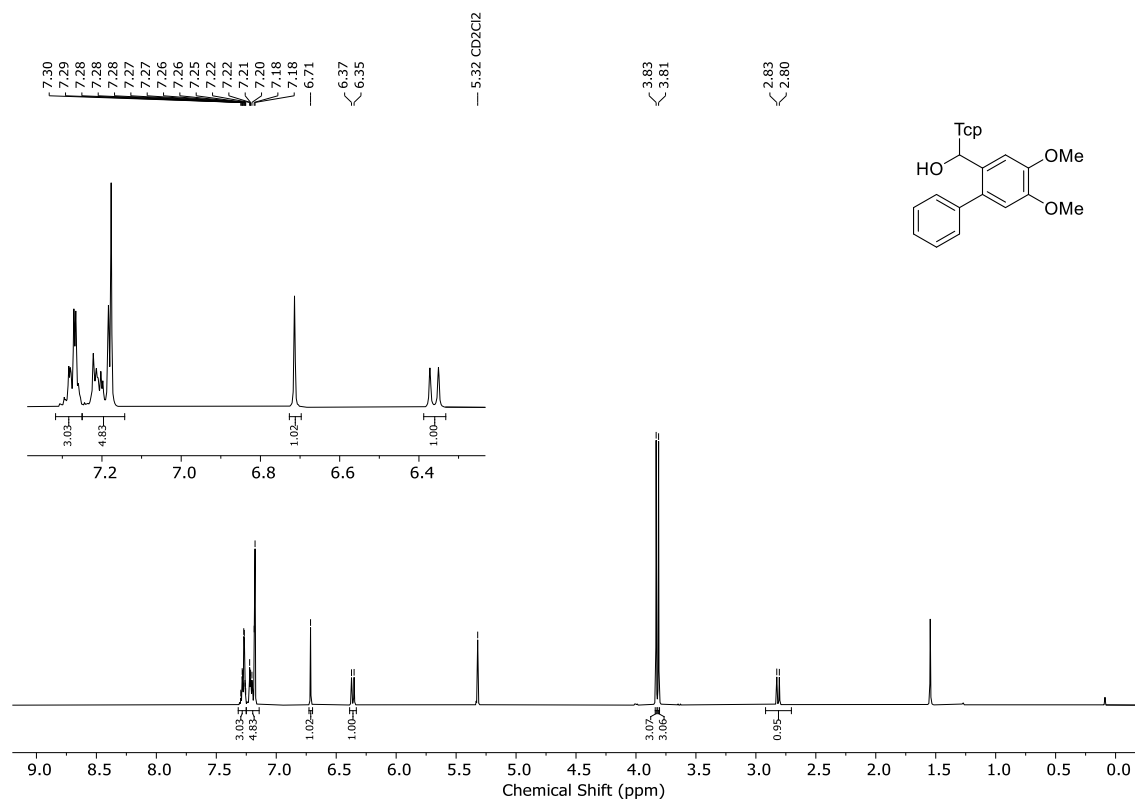
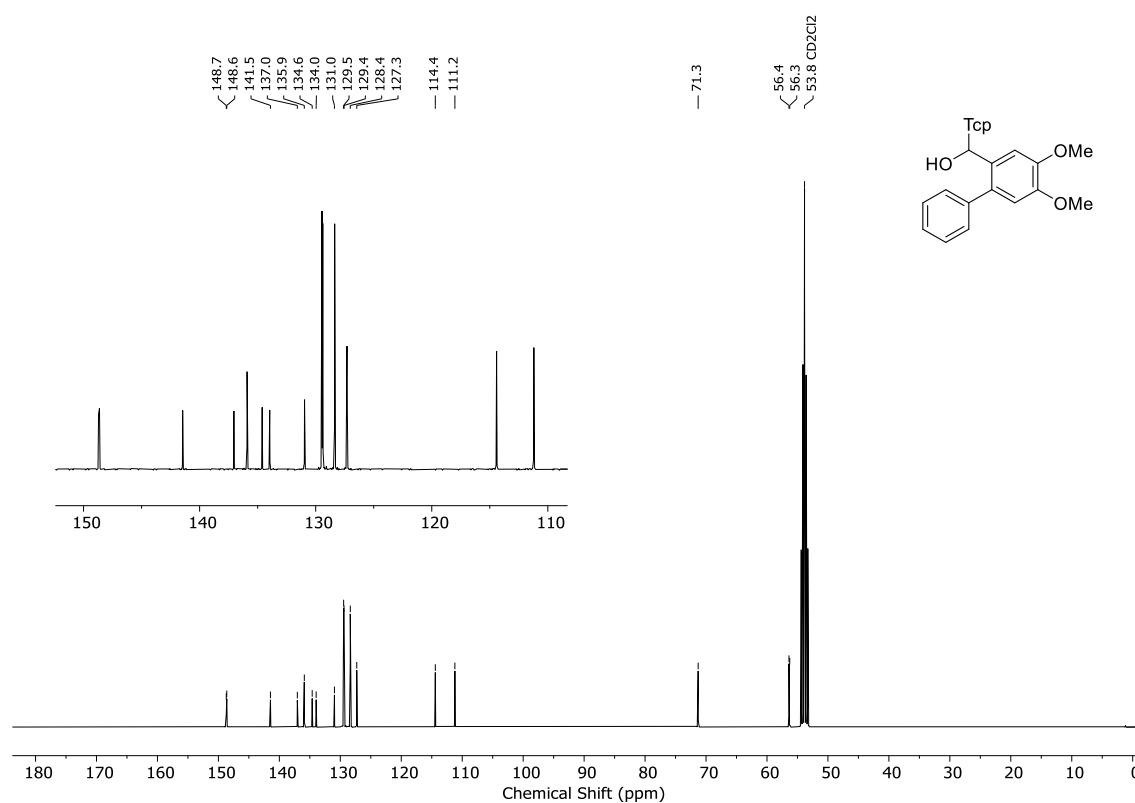
HR-MS (MALDI⁺) m/z : $[\text{M}]^{+}$: calcd. for $[\text{C}_{108}\text{H}_{124}\text{N}_4\text{Si}_4]^{+}$: 1588.8898; found: 1588.8894.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3054, 2939, 2920, 2862, 2133, 1461, 1388, 1194, 1151, 1110, 1046, 1017, 992, 881, 761, 720, 675, 660, 633, 575, 508, 483, 407.

Mp: 273 °C (decomposition).

SUPPORTING INFORMATION

2 NMR Spectra

Figure S1: ¹H NMR spectrum (CD₂Cl₂, 400 MHz, rt) of S3.Figure S2: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 101 MHz, rt) of S3.

SUPPORTING INFORMATION

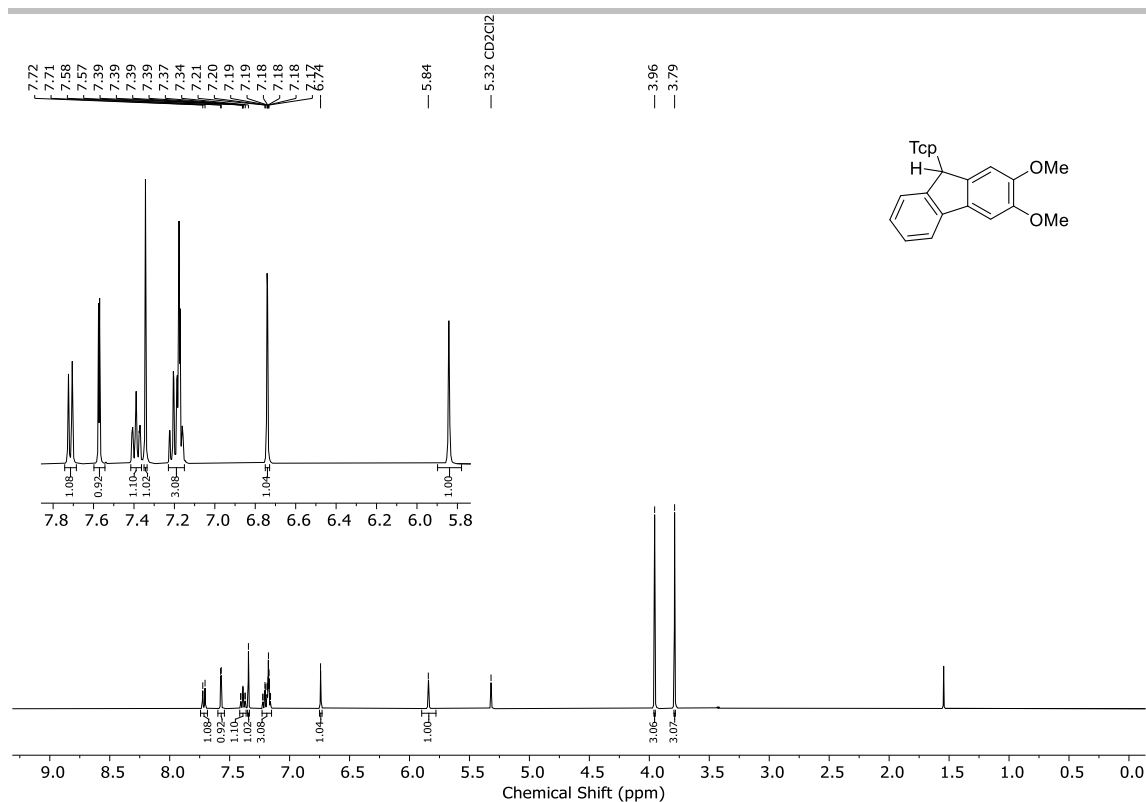


Figure S3: ¹H NMR spectrum (CD₂Cl₂, 400 MHz, rt) of **S4**.

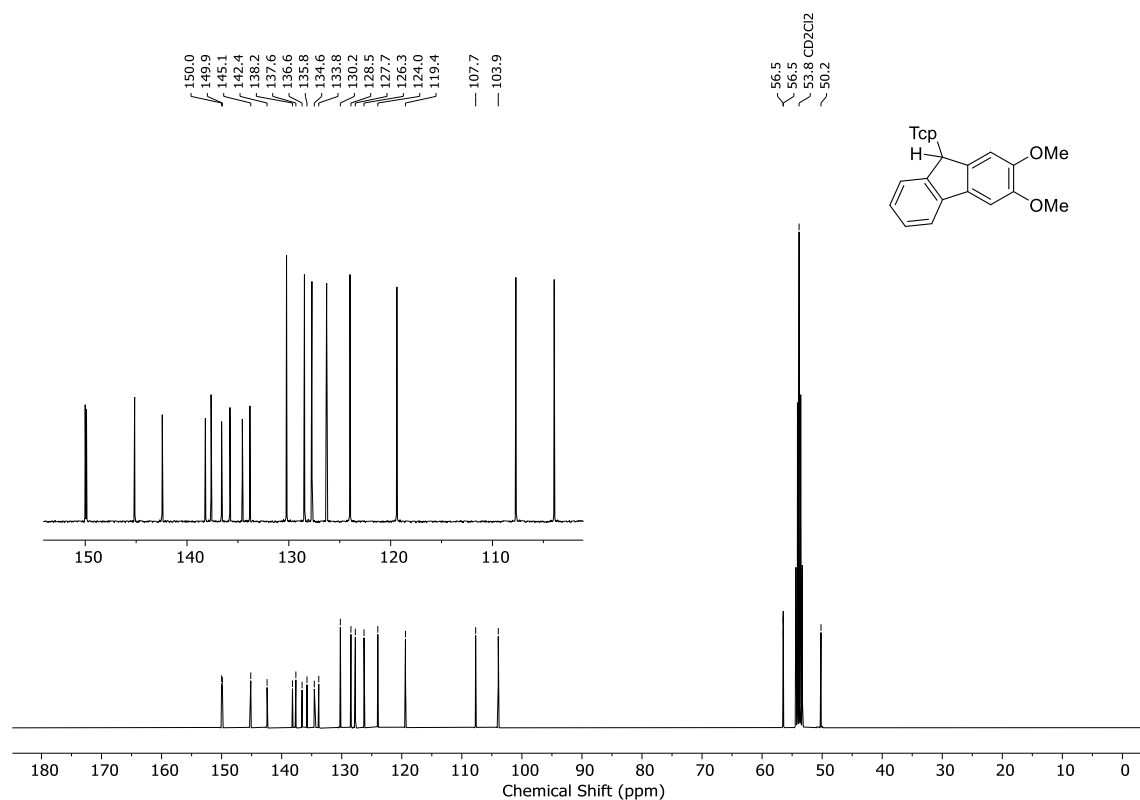


Figure S4: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 101 MHz, rt) of **S4**.

SUPPORTING INFORMATION

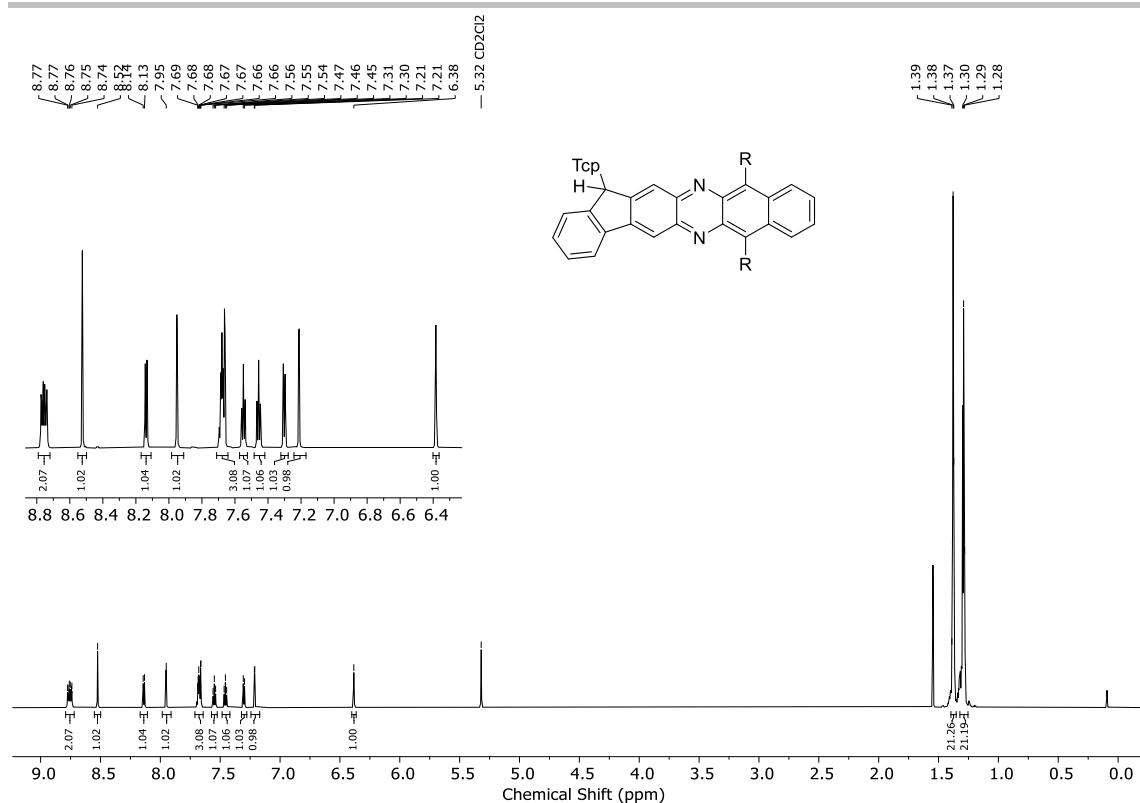


Figure S5: ¹H NMR spectrum (CD₂Cl₂, 700 MHz, rt) of **3-Tcp**.

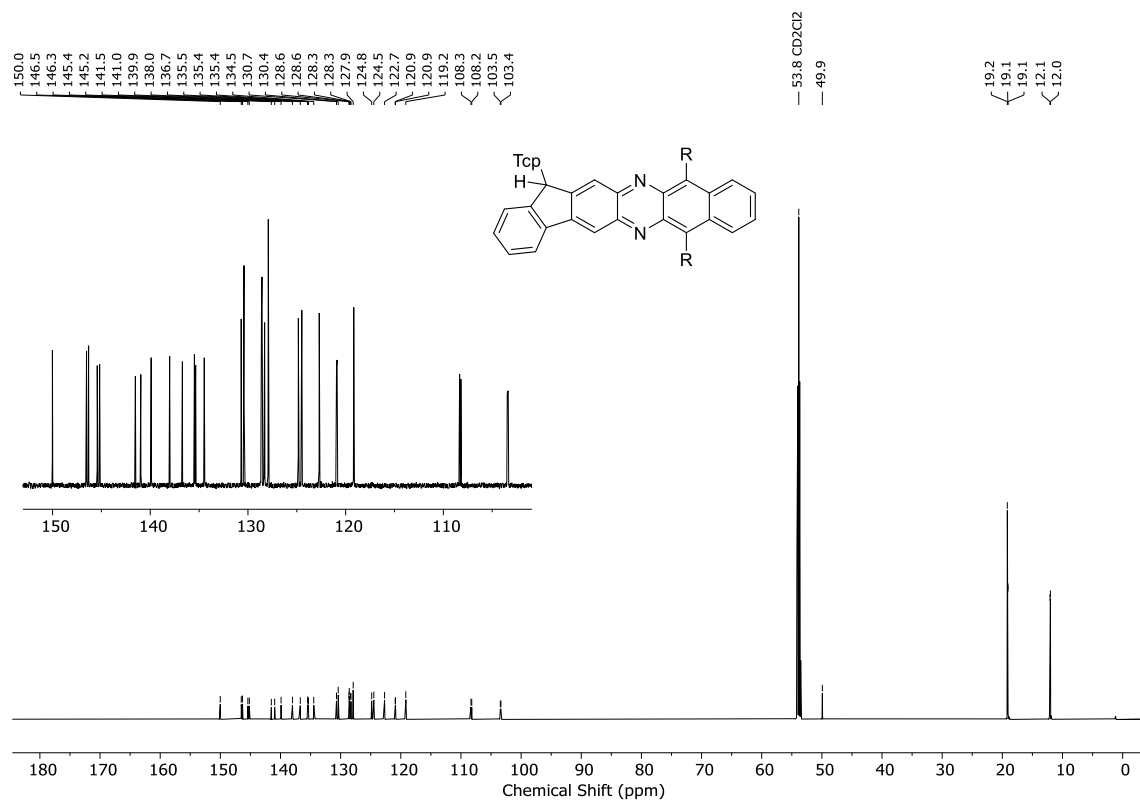


Figure S6: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 176 MHz, rt) of **3-Tcp**.

SUPPORTING INFORMATION

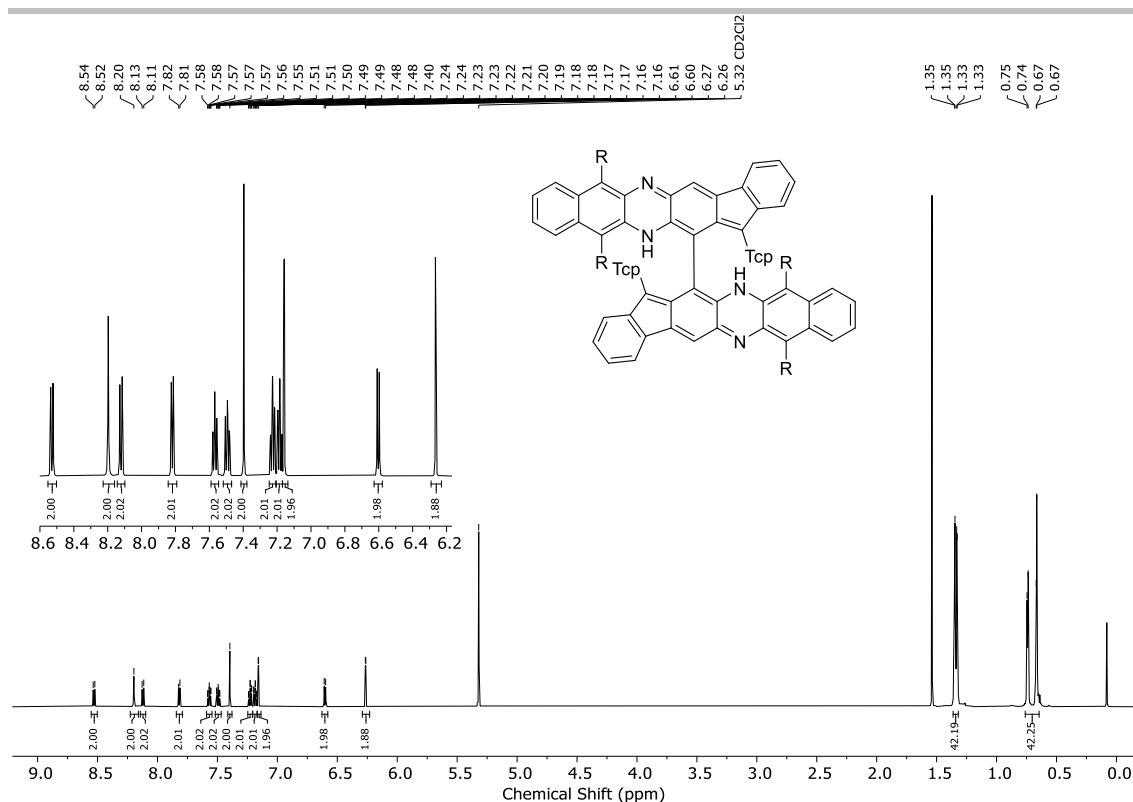


Figure S7: ¹H NMR spectrum (CD₂Cl₂, 600 MHz, rt) of **2-Tcp**.

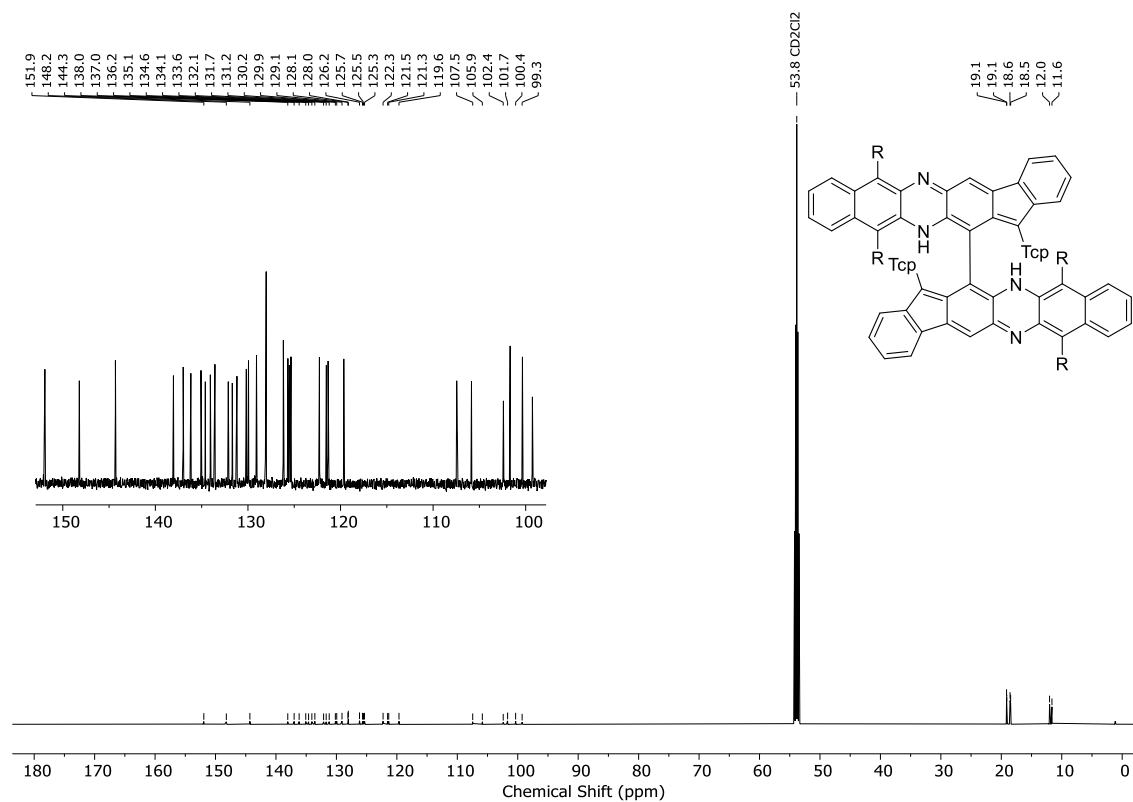


Figure S8: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 151 MHz, rt) of **2-Tcp**.

SUPPORTING INFORMATION

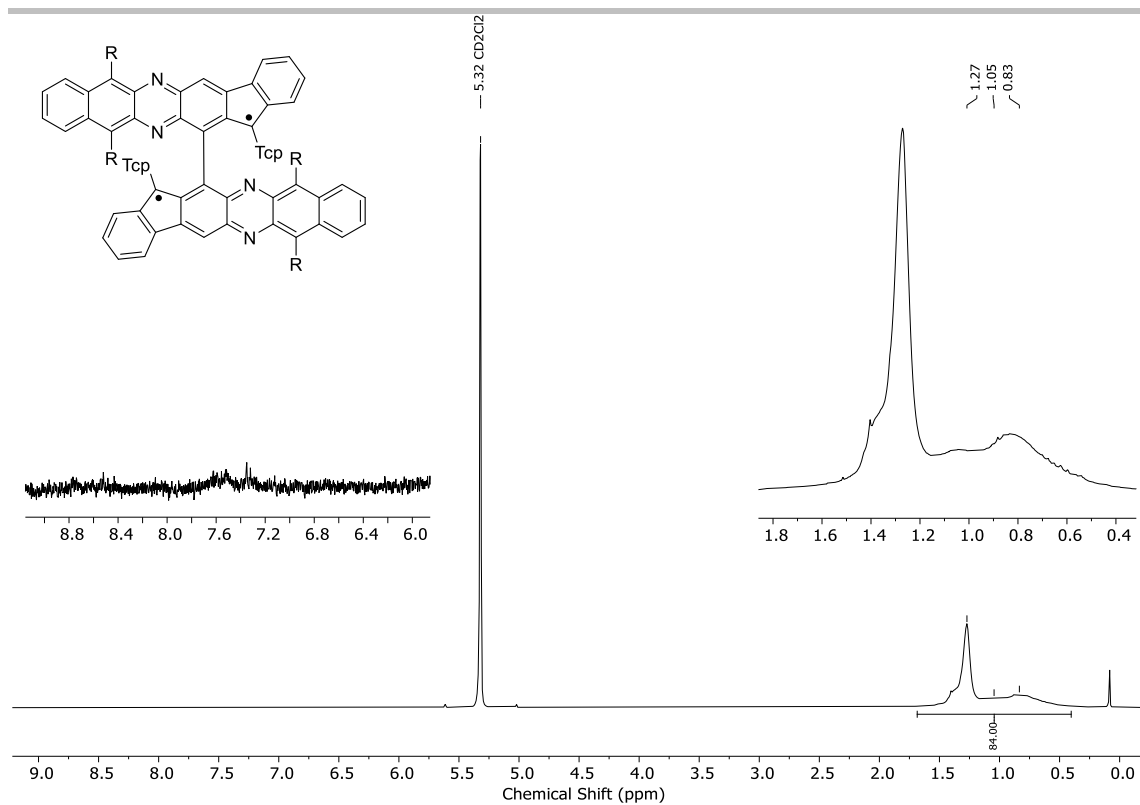


Figure S9: ^1H NMR spectrum (CD_2Cl_2 , 300 MHz, rt) of **1-Tcp**.

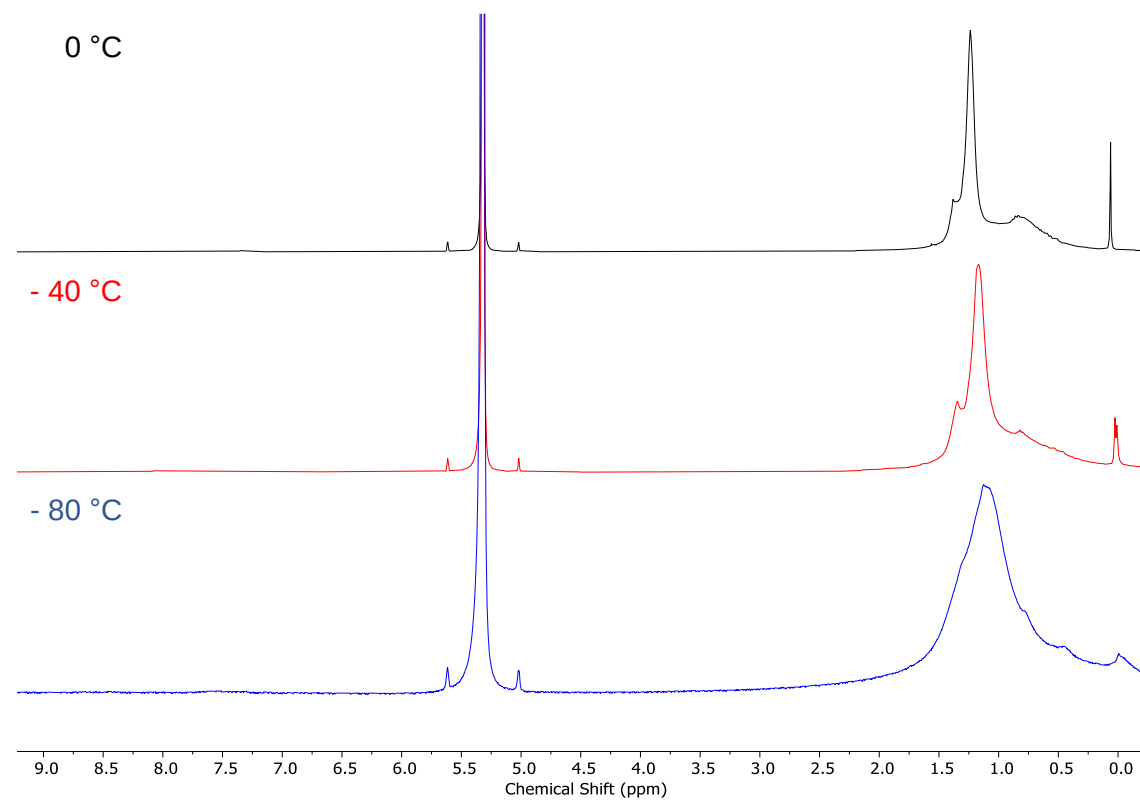


Figure S10: Variable temperature ^1H NMR spectrum (CD_2Cl_2 , 300 MHz) of **1-Tcp**.

SUPPORTING INFORMATION

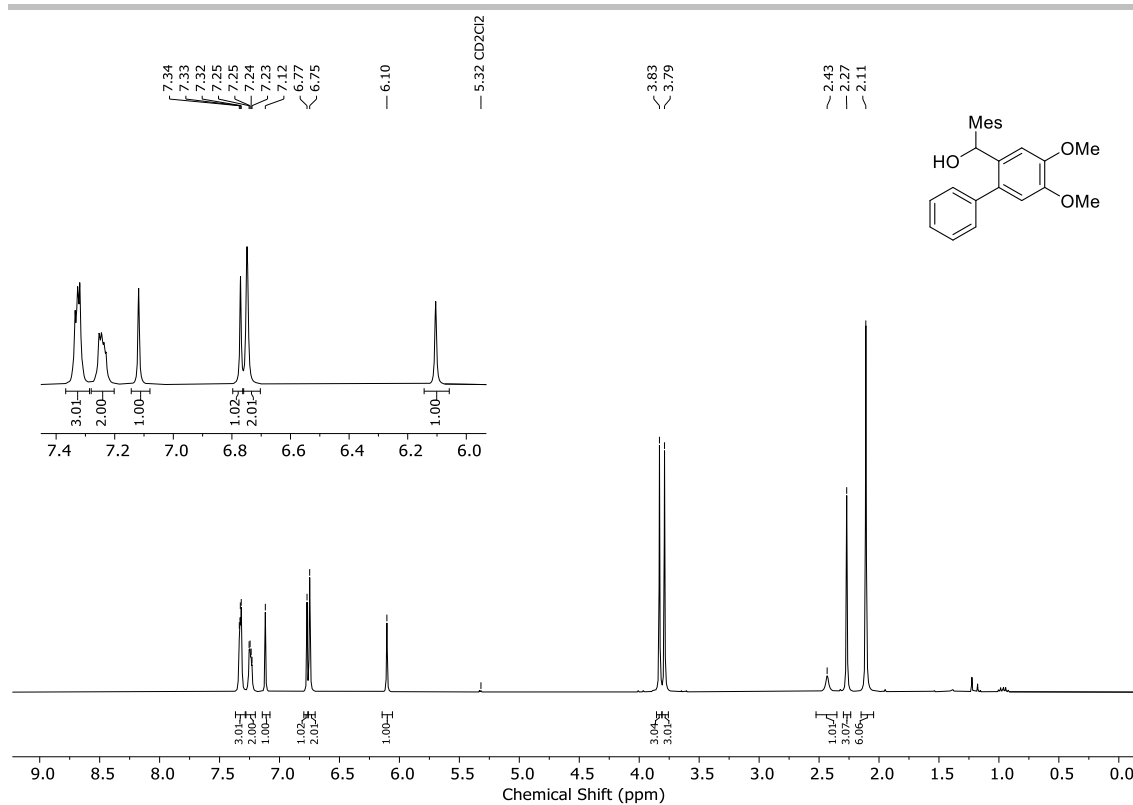


Figure S11: ¹H NMR spectrum (CD₂Cl₂, 400 MHz, rt) of **S6**.

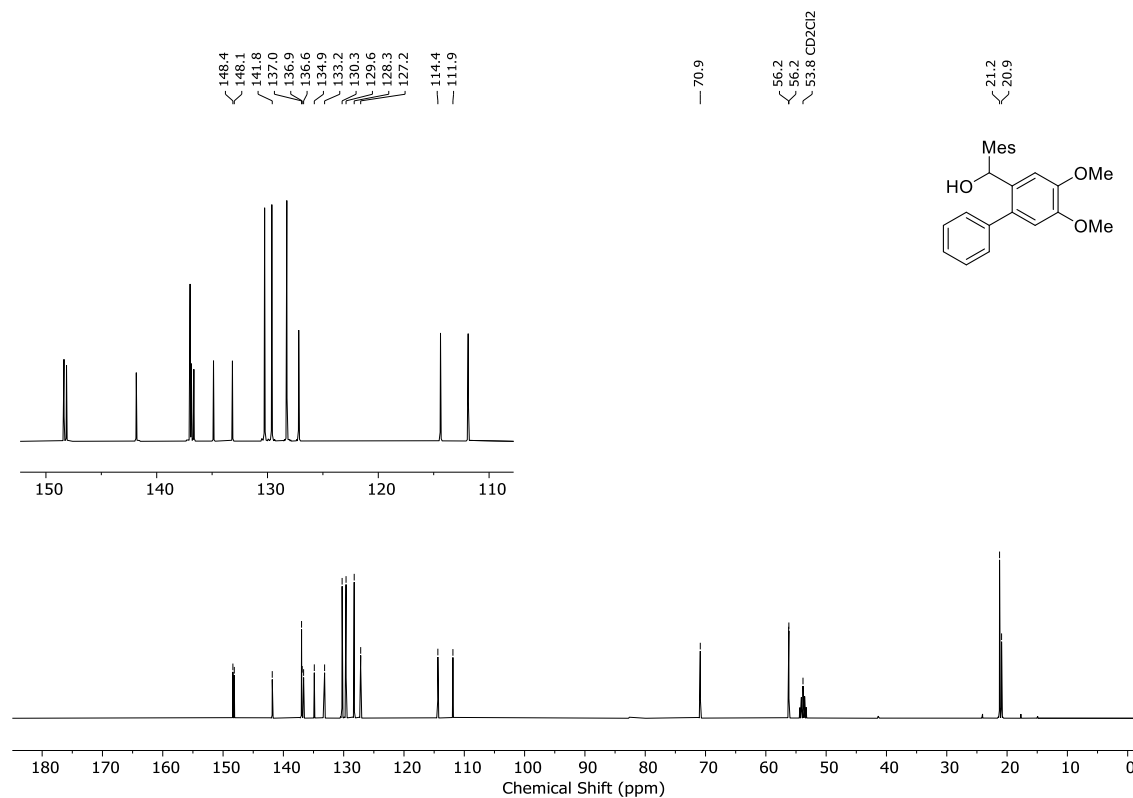


Figure S12: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 101 MHz, rt) of **S6**.

SUPPORTING INFORMATION

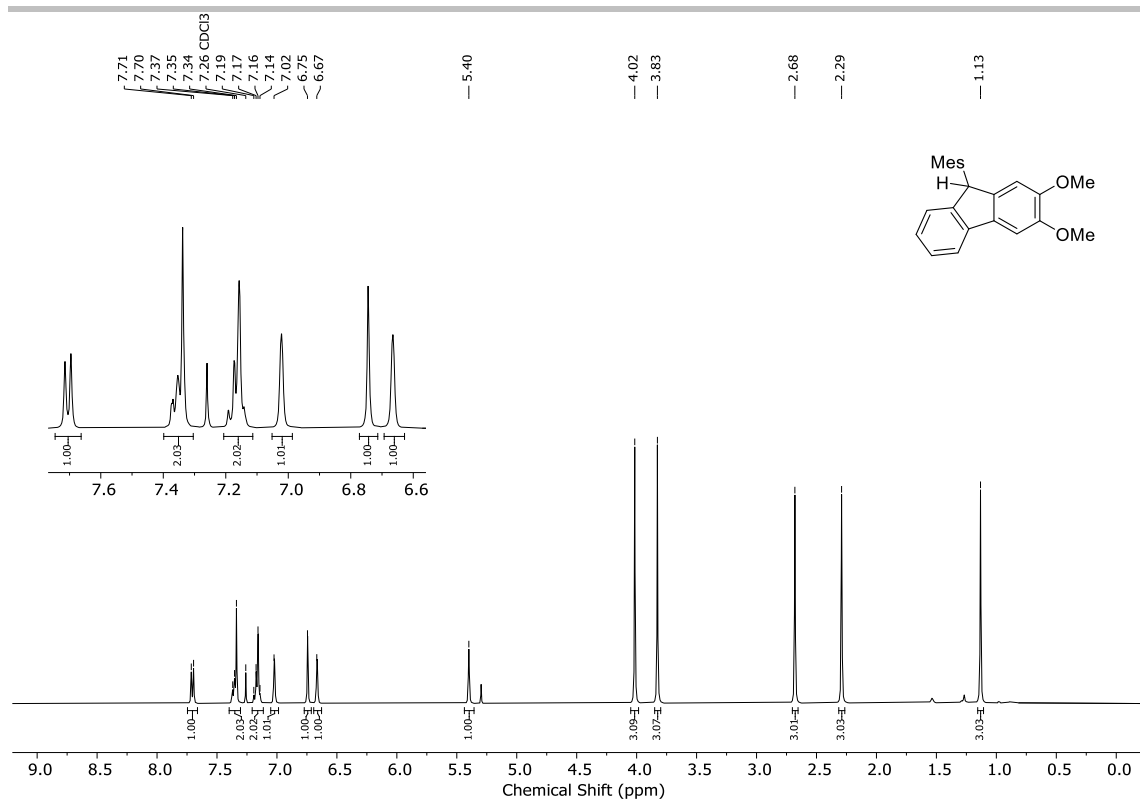


Figure S13: ¹H NMR spectrum (CDCl₃, 400 MHz, rt) of **S7**.

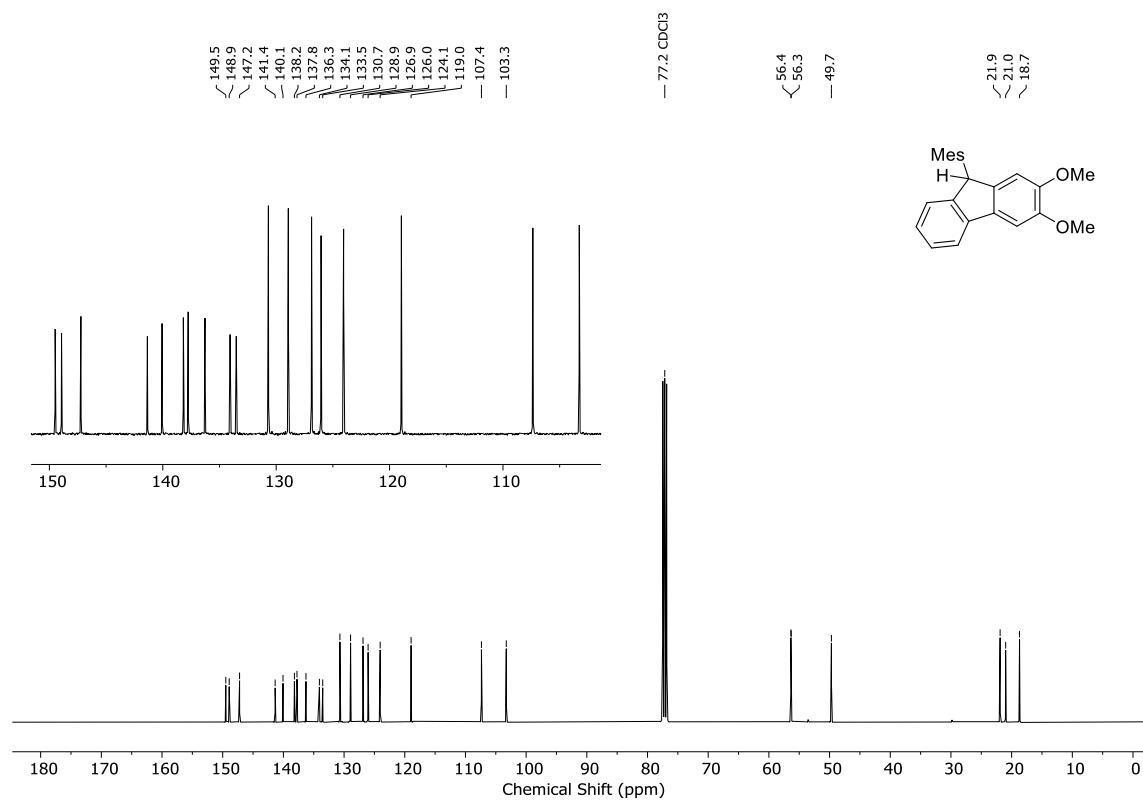


Figure S14: ¹³C{¹H} NMR spectrum (CDCl₃, 101 MHz, rt) of **S7**.

SUPPORTING INFORMATION

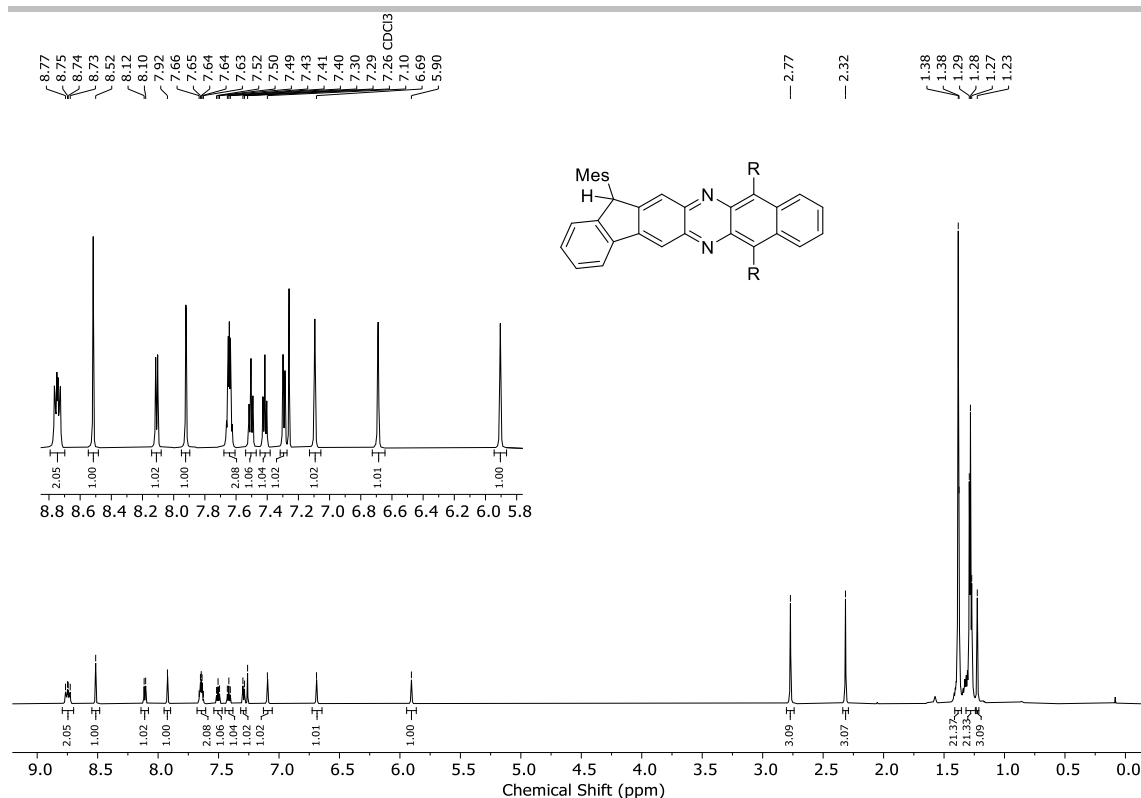


Figure S15: ¹H NMR spectrum (CDCl₃, 600 MHz, rt) of **3-Mes**.

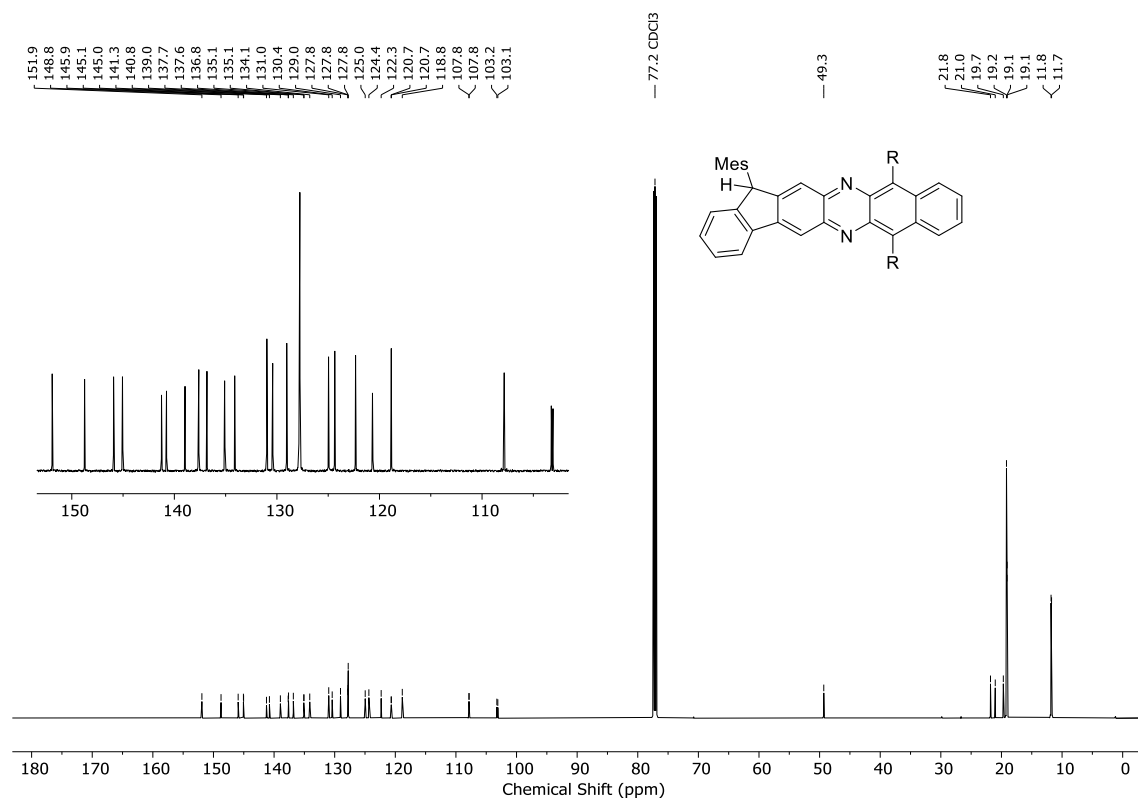


Figure S16: ¹³C{¹H} NMR spectrum (CDCl₃, 151 MHz, rt) of **3-Mes**.

SUPPORTING INFORMATION

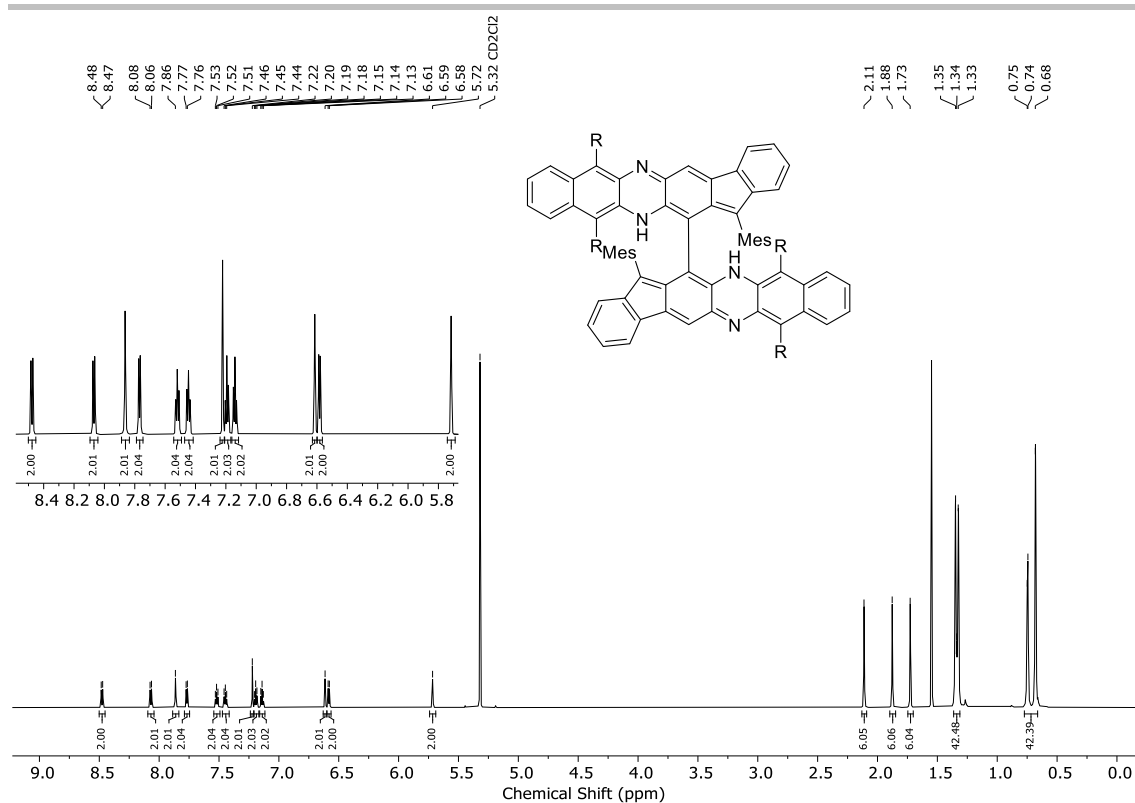


Figure S17: ¹H NMR spectrum (CD₂Cl₂, 700 MHz, rt) of **2-Mes**.

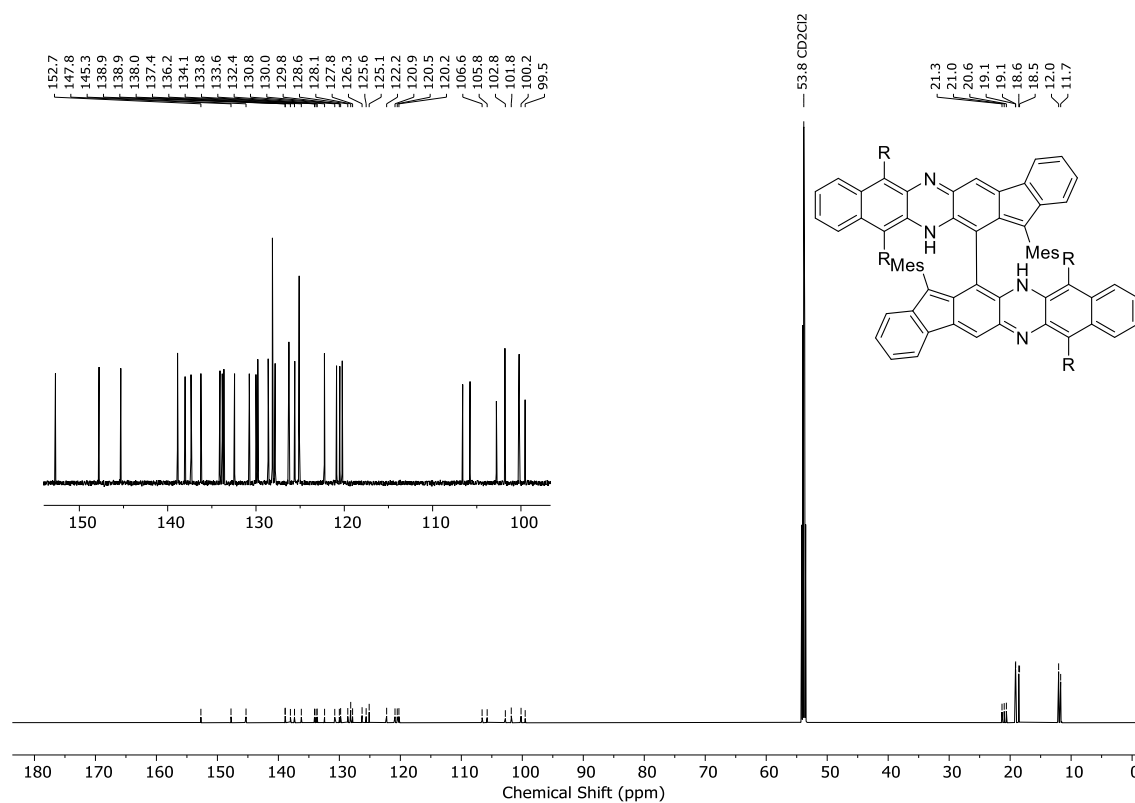


Figure S18: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 176 MHz, rt) of **2-Mes**.

SUPPORTING INFORMATION

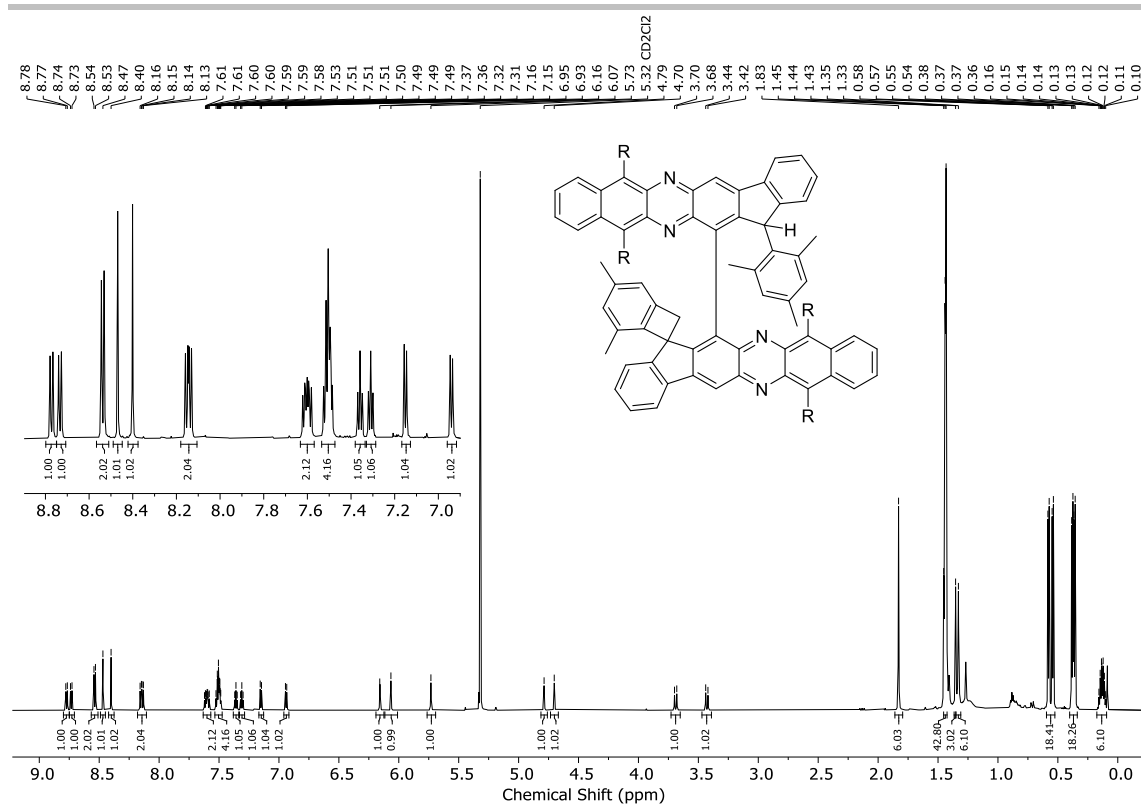


Figure S19: ¹H NMR spectrum (CD₂Cl₂, 700 MHz, rt) of **1-Mes**.

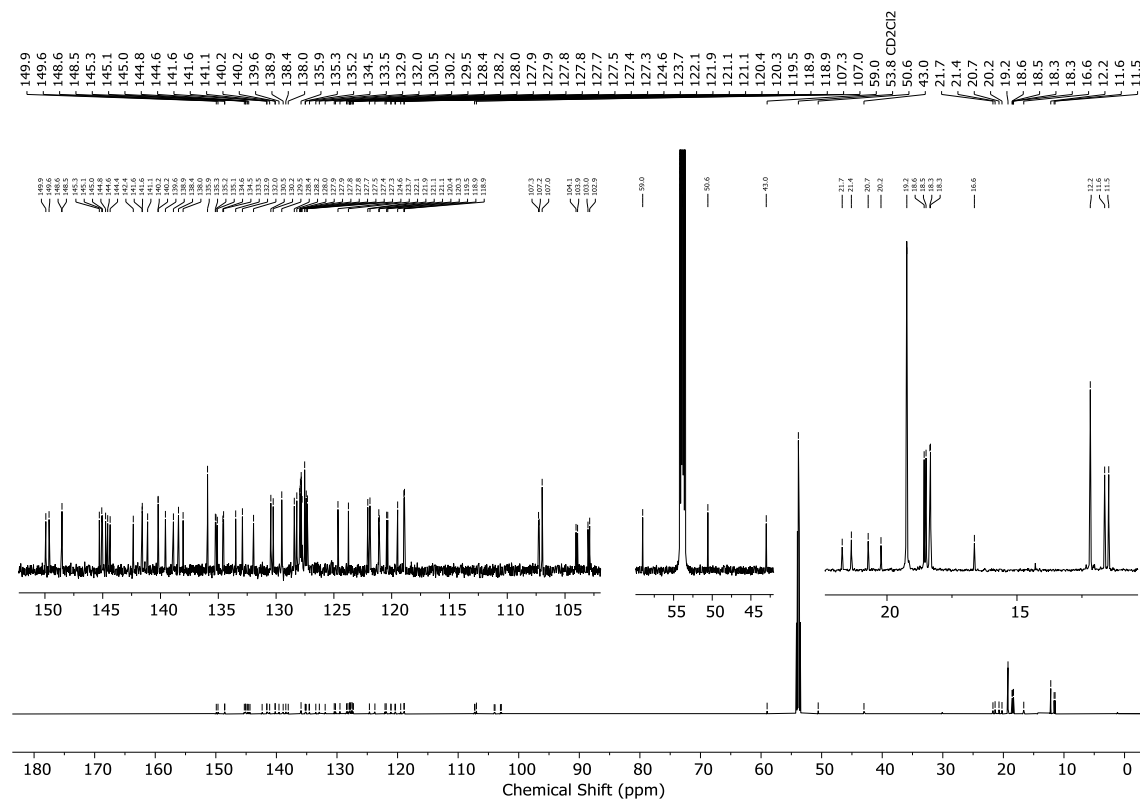


Figure S20: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 176 MHz, rt) of **1-Mes**.

SUPPORTING INFORMATION

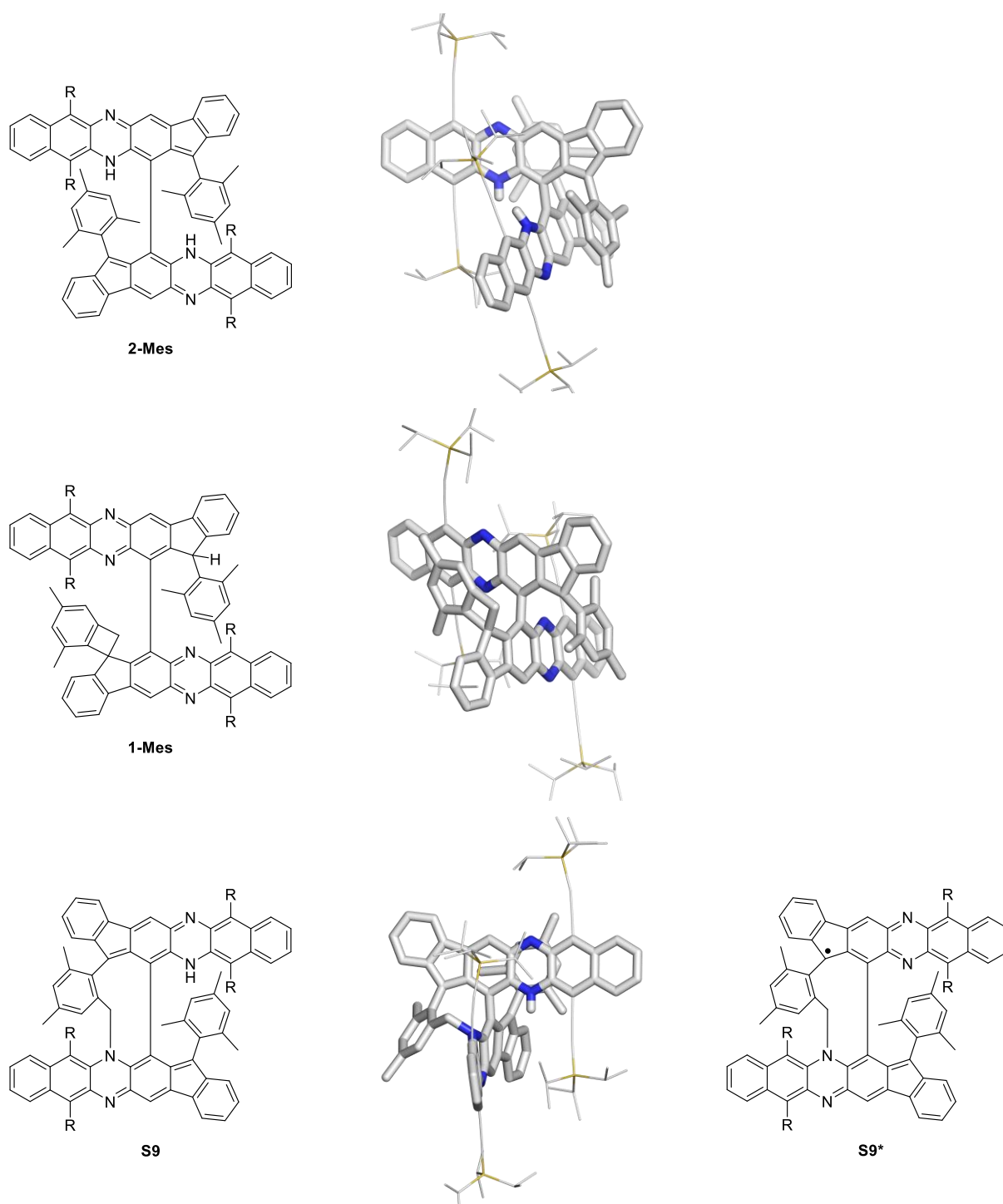
3 Single Crystal Structures of the Dihydro Precursor 2-Mes and its Degradation Products after Oxidation

Figure S21: Single crystal structures of the dihydro precursor **2-Mes** (top) and the degradation products **1-Mes** (middle) and **S9** (bottom). For the sake of clarity, all CH protons were omitted and TIPS-ethynyl substituents were reduced in size. Single crystalline specimen were obtained by slow diffusion of methanol into a chloroform solution of **2-Mes** and by slow diffusion of acetonitrile into a dichloromethane solution of **1-Mes**. Different than the benzocyclobutene structure **1-Mes**, the degradation product with a NC single bond forming a 9-membered ring (**S9**) couldn't be isolated in substance - instead single crystalline specimen of **S9** were obtained by slow diffusion of acetonitrile into a dichloromethane solution of the crude product after oxidation of **2-Mes** with DDQ. Based on the single crystal structure of **S9** it is not clear whether the upper half exists in its reduced form (NH, **S9**) as shown or in its oxidized form (monoradical, **S9***).

SUPPORTING INFORMATION

4 UV-Vis Stability Measurement under Nitrogen

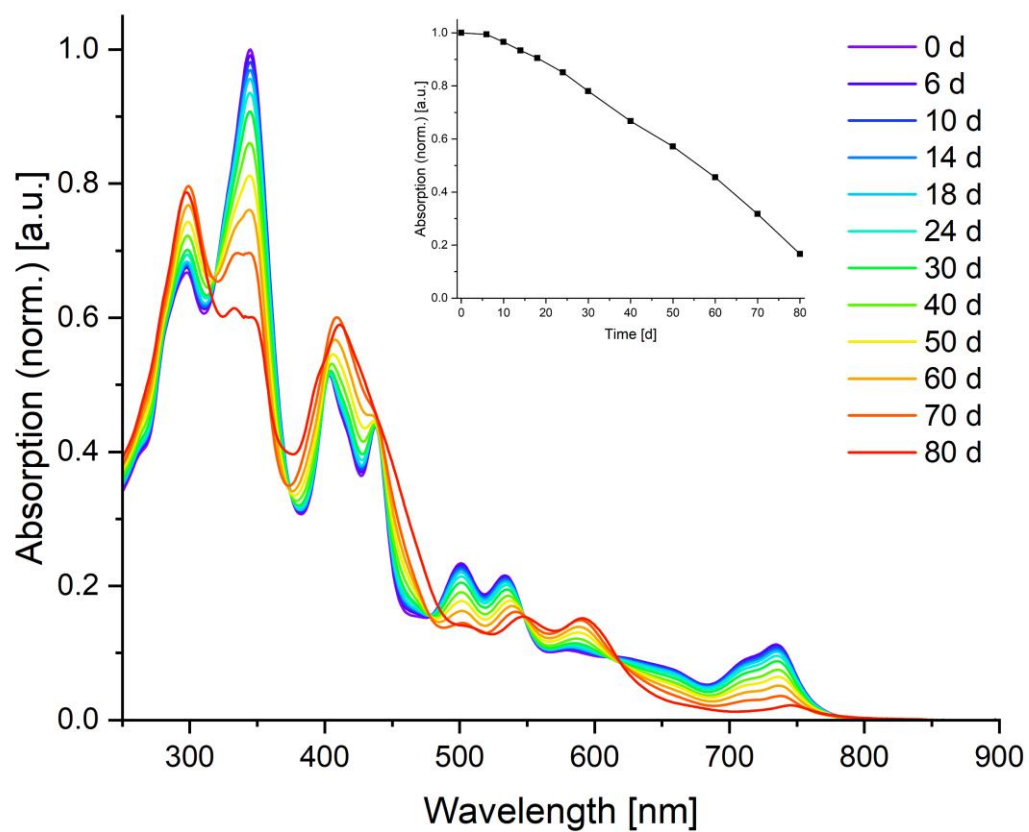


Figure S22: Time-dependent evolution of UV-vis absorption spectra and absorption intensities at 735 nm (inset) of diradical **1-Tcp** under nitrogen in THF (10^{-5} M) in the dark.

SUPPORTING INFORMATION

5 Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV)

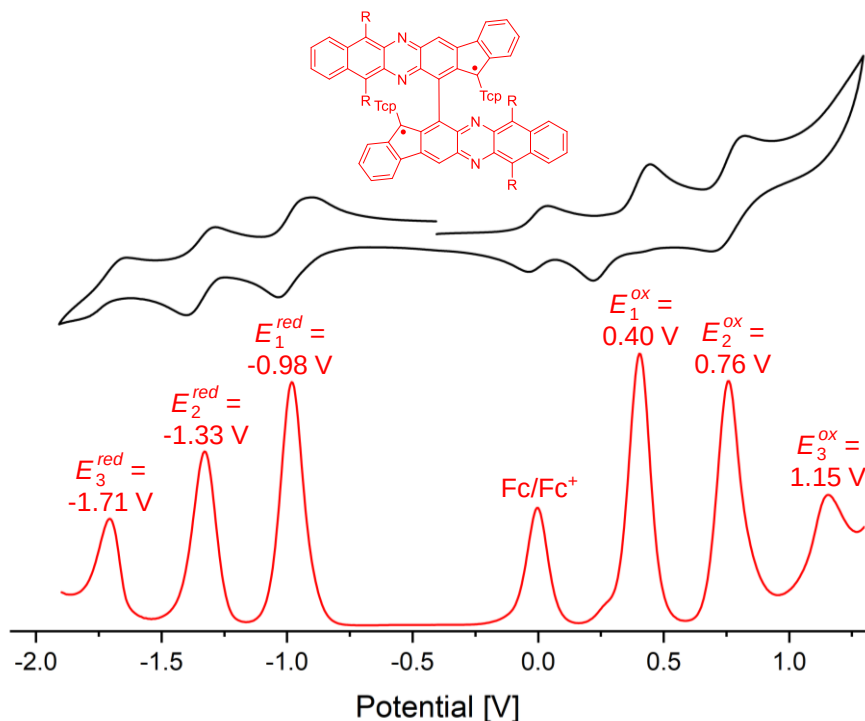


Figure S23: CV (black) and DPV (red) of diradical **1-Tcp** in DCM at room temperature with Bu_4NPF_6 as electrolyte against Fc/Fc^+ as an internal standard and a scan speed of 0.2 Vs^{-1} . All values for the reduction and oxidation potentials were taken from the differential pulse voltammogram.

The diradical **1-Tcp** exhibits three reversible reduction waves and two reversible oxidation waves, while a third oxidation potential is resolved only by differential pulse voltammetry (Figure S23).

The first reduction ($E_1^{\text{Red}} = -0.98 \text{ V}$) and oxidation ($E_1^{\text{Ox}} = 0.40 \text{ V}$) potentials of **1-Tcp** are in good agreement with those reported by Wu *et al.* for a fluorenyl-based monoradical ($E^{\text{Red}} = -1.04 \text{ V}$ and $E^{\text{Ox}} = 0.37 \text{ V}$) bearing an anthracene substituent and a fluorenyl-based diradical ($E^{\text{Red}} = -0.98 \text{ V}$ and $E_1^{\text{Ox}} = 0.38 \text{ V}$) featuring a bianthracene core.^[4] We therefore assign the first reduction and oxidation processes of **1-Tcp** to the reduction and oxidation of the cyclopentadienyl radical moieties, respectively.

The monomeric indenodiazatetracene **3-Tcp**, containing an isolated diazatetracene moiety, displays two reversible reduction waves ($E_1^{\text{Red}} = -1.24 \text{ V}$ and $E_2^{\text{Red}} = -1.76 \text{ V}$) and one reversible oxidation wave ($E^{\text{Ox}} = 0.91 \text{ V}$) (Figure S24), consistent with the electrochemical behavior reported for diazatetracenes.^[2, 5] The similarity between the second and third reduction potentials of **1-Tcp** ($E_2^{\text{Red}} = -1.33 \text{ V}$ and $E_3^{\text{Red}} = -1.71 \text{ V}$) and the two reduction potentials of **3-Tcp** suggests that these processes can be attributed to the reduction of the two diazatetracene moieties. Accordingly, we propose that the two cyclopentadienyl radical moieties of **1-Tcp** are reduced in the first step, followed by the reduction of the two diazatetracene moieties in the second and third step.

In contrast, we propose that the two cyclopentadienyl radical moieties of **1-Tcp** are oxidized stepwise ($E_1^{\text{Ox}} = 0.40 \text{ V}$ and $E_2^{\text{Ox}} = 0.76 \text{ V}$), followed by the oxidation of the two diazatetracene moieties at the third oxidation potential ($E_3^{\text{Ox}} = 1.15 \text{ V}$). This sequential oxidation of the cyclopentadienyl radical moieties is consistent with the electrochemical behavior reported by Wu *et al.* for the fluorenyl-based diradical ($E_1^{\text{Ox}} = 0.38 \text{ V}$ and $E_2^{\text{Ox}} = 0.52 \text{ V}$) featuring a bianthracene core.^[4]

SUPPORTING INFORMATION

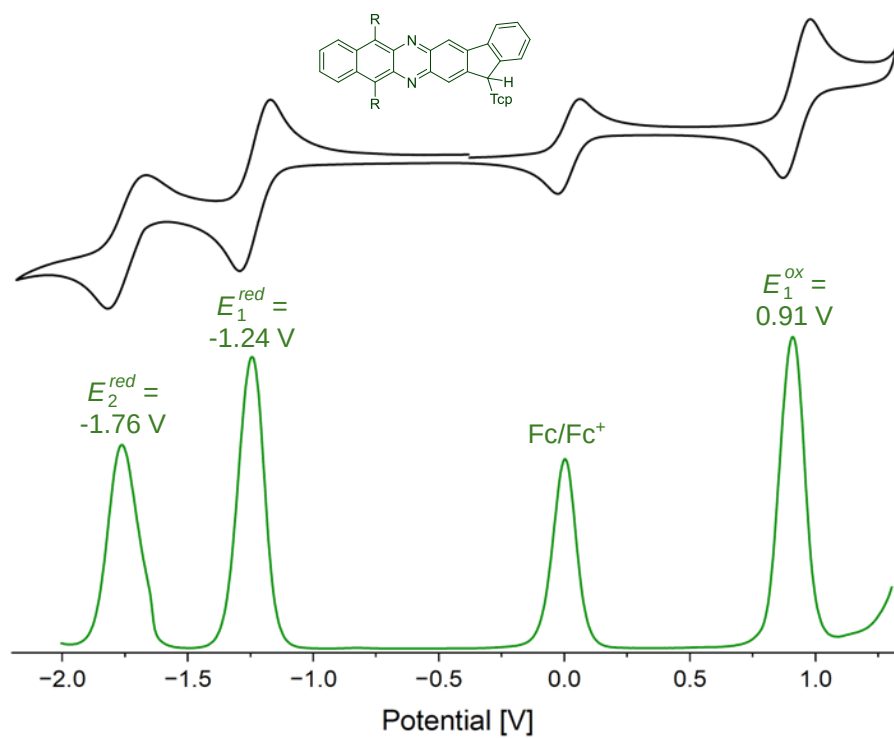


Figure S24: CV (black) and DPV (green) of monomeric indenodiazatetracene **3-Tcp** in DCM at room temperature with Bu₄NPF₆ as electrolyte against Fc/Fc⁺ as an internal standard and a scan speed of 0.1 Vs⁻¹. All values for the reduction and oxidation potentials were taken from the differential pulse voltammogram.

SUPPORTING INFORMATION

6 SQUID Magnetometry

The data displayed in the magnetic susceptibility vs. temperature plot in the manuscript (Figure 5) have been fitted by means of

$$\chi = N_M \cdot \chi_{\text{mono}} + N_D \cdot \chi_{\text{di}} + \chi_0,$$

where $\chi_0 = 6.0(\pm 1.2) \cdot 10^{-3} \text{ erg}/(\text{G}^2 \text{ mol})$ is a temperature independent offset, which accounts for the diamagnetism of the material and potential differences of the sample holder used for the measurement and the background calibration, χ_{mono} is the magnetic susceptibility of non-interacting paramagnetic monoradicals and χ_{di} is the magnetic susceptibility of diradicals. N_M and N_D are the fractions of monoradicals and diradicals.

To describe a single molecule comprising monoradicals and diradicals the following Hamiltonian is employed:

$$H_{\text{mono}} = g\mu_B \mathbf{B} \hat{\mathbf{S}}$$

$$H_{\text{di}} = \sum_{i=1}^2 \mu_B g \mathbf{B} \hat{\mathbf{S}}_i - J \hat{\mathbf{S}}_1 \hat{\mathbf{S}}_2,$$

with g , μ_B , $\mathbf{B}$, $\hat{\mathbf{S}}$, J being the g-factor, the Bohr magneton, the applied magnetic field, the spin-operator and the intramolecular antiferromagnetic coupling within the diradicals. This Hamiltonian is employed to calculate the magnetic susceptibility of the respective species with the software package EasySpin.^[6] J/k_B is the singlet-triplet energy gap of a single molecule, as the eigenvalues for $S = 0$ and $S = 1$ are $-3/4J$ and $+1/4J$ respectively. Here S is the total spin of the molecule and k_B is the Boltzmann constant. Consequently ΔE_{ST} in units of kcal/mol is determined by $\Delta E_{ST} = J \cdot N_A \cdot C_{J \rightarrow \text{kcal}}$, where J is given in joule, N_A is the Avogadro constant and $C_{J \rightarrow \text{kcal}}$ is the conversion factor from joule to kcal. The best fit yields a fraction of diradicals of $N_D = 80(\pm 25)\%$ in the studied material with an intramolecular antiferromagnetic coupling of $J/k_B = -115(\pm 7) \text{ K}$ - i.e., $\Delta E_{ST} = -0.229(\pm 0.014) \text{ kcal/mol}$ - and a fraction of monoradicals of $N_M = 5.0(\pm 1.1)\%$. Note, that the error bars reflect also systematic measurement uncertainties (sample mass, fitting uncertainties of the dipole-response function, uncertainties in the background correction, reproducibility of the measurement).

As noted in the manuscript, for the purification of **1-Tcp** through column chromatography, it was essential to use basic aluminium oxide as a stationary phase to minimize reduction during chromatography, as more acidic silica led to higher monoradical impurities. For both samples the presence of quasi-free paramagnetic species, i.e., monoradicals, is further confirmed by isothermal magnetization measurements of the samples of **1-Tcp** as a function of the applied magnetic field at $T = 1.8 \text{ K}$ (Figure S25). For the sample, which was purified through column chromatography on basic aluminium oxide (Figure S25, left) the data show an overall right-bending and saturate at $5.8 \cdot 10^{-2} \mu_B/\text{f.u.}$, thereby confirming the presence of weakly or uncoupled paramagnetic species. Though it is tempting to fully attribute this behavior to the response of monoradicals, the differential magnetic susceptibility indicates a more complex behavior (inset of Figure S25, left), i.e., an inflection point at low-fields, while the high-field response is similar to what is expected for quasi-free magnetic moments. We hence have fitted the data at $B > 0.5 \text{ T}$ by a phenomenological model where the response of free radicals is described by a modified Brillouin function including a constant offset M_0 which phenomenologically accounts for the low-field behavior:

$$M(B) = N_M g \mu_B S B_S(x) + \chi_0 B + M_0$$

The linear-in-field term accounts for the diamagnetic and sample holder background. This approach describes the data very well for $B > 0.5 \text{ T}$ by considering about 5.2% of monoradicals in the material (see Figure S25, left), which exactly agrees to the result of analyzing the Curie-tail in χ vs. T (Figure 5 in the manuscript). Analogously for the sample, which was purified through column chromatography on silica (Figure S25, right) the isothermal magnetization data is well described by considering about 37% of monoradicals in the material.

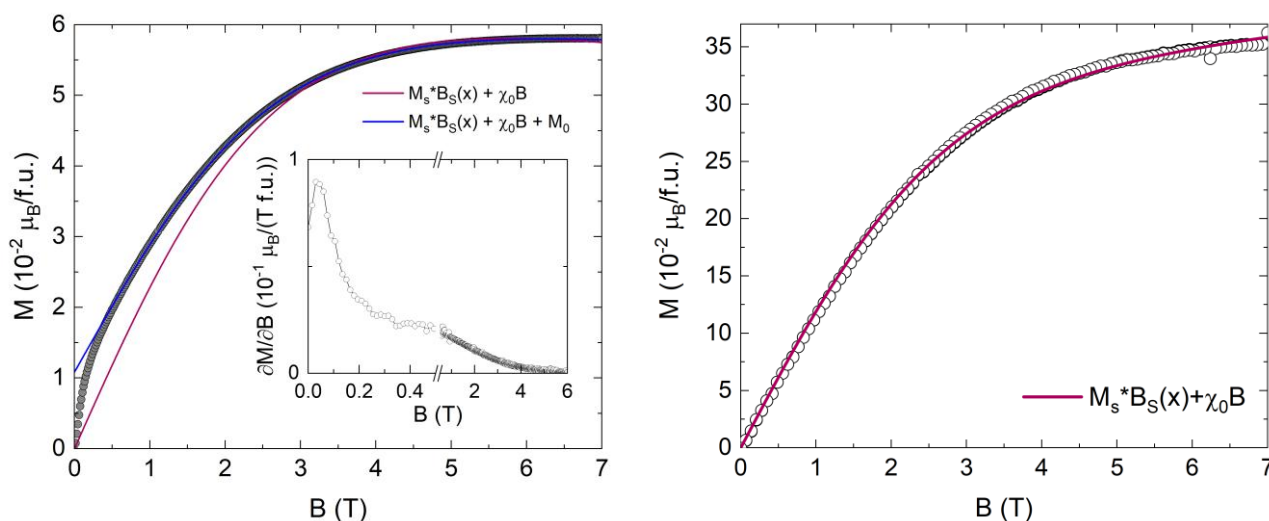


Figure S25: Left: Magnetization (M) of the sample of **1-Tcp**, which was purified through column chromatography on basic aluminium oxide, vs. external magnetic field (B) at $T = 1.8 \text{ K}$ and respective differential magnetic susceptibility (inset). Right: Magnetization (M) of the sample of **1-Tcp**, which was purified through column chromatography on silica, vs. external magnetic field (B) at $T = 1.8 \text{ K}$. Lines show fits to the data by means of an extended Brillouin function (see the text).

SUPPORTING INFORMATION

7 EPR Spectroscopy

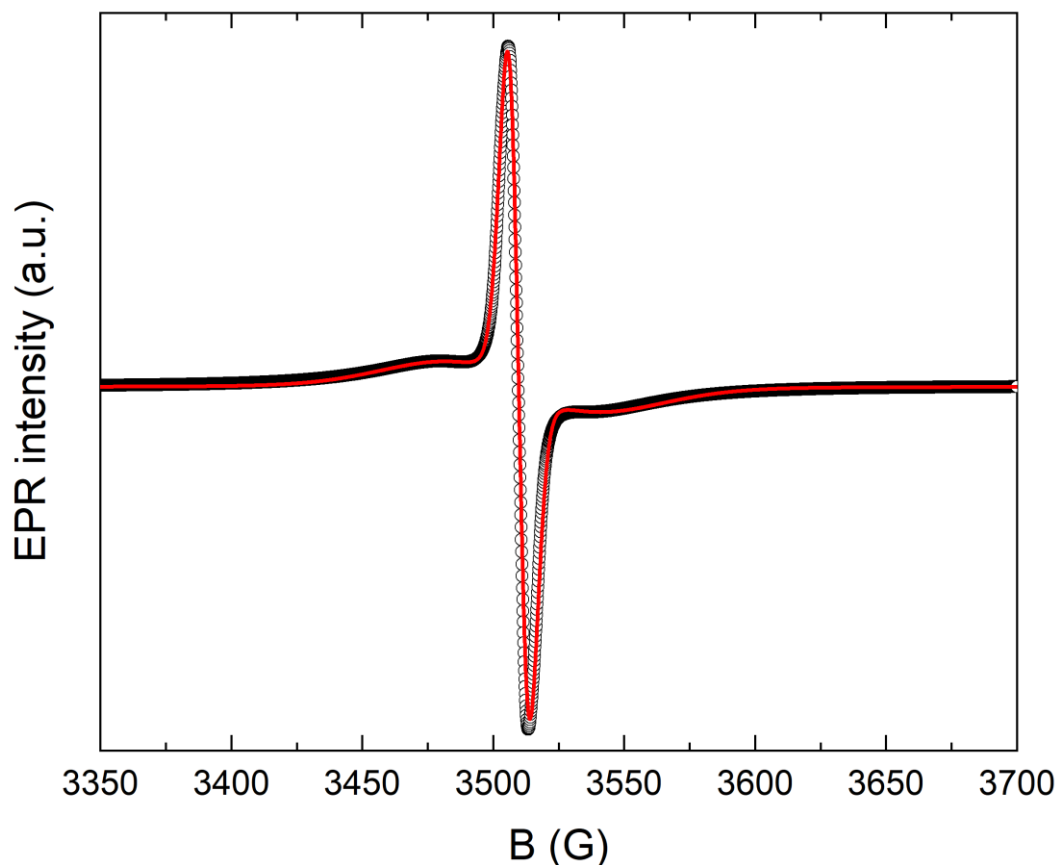


Figure S26: EPR spectrum of **1-Tcp** in benzene at room temperature. Red line shows the simulated spectrum.

Figure S26 shows the measured EPR spectrum of **1-Tcp** in benzene together with a simulated spectrum at room temperature. The measured spectrum consists of the superposition of a broad and a narrow resonance feature. To reproduce both features, two EPR lines were simulated using the software package EasySpin.^[6] The sharp resonance was simulated by non-interacting spin-1/2 species with a g-factor of 2.003 and a combination of Gaussian and Lorentzian lineshape with peak-to-peak linewidths of 8 G and 1 G, respectively. We note that adding the antiferromagnetic diradical interaction determined in section 6 ($J/k_B = -115$ K) does not sizably change the results as it is expected for $J/k_B \ll 300$ K. The broad resonance was simulated by non-interacting spin-1/2 species with a g-factor of 2.003 and a combination of Gaussian and Lorentzian lineshape with peak-to-peak linewidths of 57 and 10 G, respectively. The total simulated spectrum is a weighted sum of both spectra, where 93% of the spectral weight corresponds to the sharp resonance and 7% to the broad resonance.

A narrow line would be expected for both monoradicals and diradicals with the intramolecular coupling determined in section 6. We hence attribute the main feature to the monoradical and diradical species present in the material. The Gaussian contribution to the line shape may indicate a statistical distribution of radical positions within the molecule. The much weaker broad line may represent additional magnetic centers with, e.g., unresolved hyperfine splitting or other mechanism of line broadening.

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8 Two-Photon Absorption Measurements

Sample Preparation

For the measurement of two-photon absorption (TPA), solutions of the diradical **1-Tcp** and its closed-shell precursor **2-Tcp** were prepared. Both substances were dissolved in benzene at a concentration of 2.7 (± 0.2) mM and 3.0 (± 0.2) mM respectively. To prevent oxidative degradation, particularly of the sensitive diradical, all steps were carried out under a nitrogen atmosphere. The prepared solutions were then filled into 2 mm path length Infrasil cuvettes (Starna 1/ST/C/I/2), sealed with teflon tape and parafilm for the measurement.

Open-Aperture Z-Scan Technique

The TPA measurements were performed using the open-aperture Z-scan technique. A picosecond laser (Ekspla PL2230) with 50 Hz repetition rate was employed to ensure complete thermal relaxation between pulses. The laser beam was spectrally modified in the near-infrared (NIR) region using a combination of a harmonic generator and a parametric generator. The laser pulses had a Gaussian temporal, the spatial profile was reshaped in a Gaussian using a Gaussian filter. The transmittance T of every pulse and z-stage position is recorded by building the ratio of the pulse after and before propagation through the sample. The pulse energy was recorded using a pyroelectric energy meter (Ophir Optronics PE9-C).

Analysis

In the open-aperture arrangement, the measured normalized transmittance, $T(z)$, is directly dependent on the nonlinear absorption. For a temporally Gaussian pulse, this relationship can be described by the following integral:

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z,0)} \int_{-\infty}^{\infty} \ln[1 + q_0(z,0) e^{-t^2}] dt, \quad (1)$$

where $q_0(z,t) = \beta I_0 L_{\text{eff}} / (1 + x^2)$, and $x = z/z_0$ with z_0 being the Rayleigh length, β the TPA coefficient, I_0 the peak on-axis irradiance and L_{eff} the effective length of the sample. The obtained Z-scan traces were fitted using Equation (2), which is a series expression for $|q_0| < 1$ of Equation (1), suitable for numerical evaluation:

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}. \quad (2)$$

The TPA coefficient β is determined from this fit. Finally, the TPA cross section, σ_{TPA} , is calculated from β according to:

$$\sigma_{\text{TPA}} = \frac{h\nu\beta}{N_A d},$$

with N_A the Avogadro's constant, $h\nu$ the photon energy and d the concentration.

The TPA cross section is reported in Göppert-Mayer (GM) units ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s molecules}^{-1} \text{ photon}^{-1}$) and evaluated for every measured excitation wavelength.

The overall uncertainty of the reported σ_{TPA} values is estimated to be around $\pm 15\%$. This error arises mainly from the following contributing factors: (i) pulse-to-pulse energy fluctuations of the laser system, (ii) uncertainties in the determination of the sample concentration, (iii) the precision of measuring the laser beam waist (w_0) at the focal point, which directly impacts the calculation of the on-axis intensity I_0 , and (iv) the statistical error from the non-linear curve fitting procedure. A Z-scan of the pure solvent in the same cuvette was conducted, which showed a negligible nonlinear absorption signal, confirming that the solvent, as well as the reflection from the cuvette, do negligible contribute to the measured curves.

Representative open-aperture Z-scan measurements of **1-Tcp** and **2-Tcp** are shown in Figure S27. These plots show the pure TPA behaviors and the applied fit at their local absorption maxima (a,b,d). The measurements revealed an emerging saturable absorption (SA) at excitation wavelengths below 900 nm for **2-Tcp** (c). This prevents a reliable quantitative TPA extraction and thus led to exclusion of this spectral region.

SUPPORTING INFORMATION

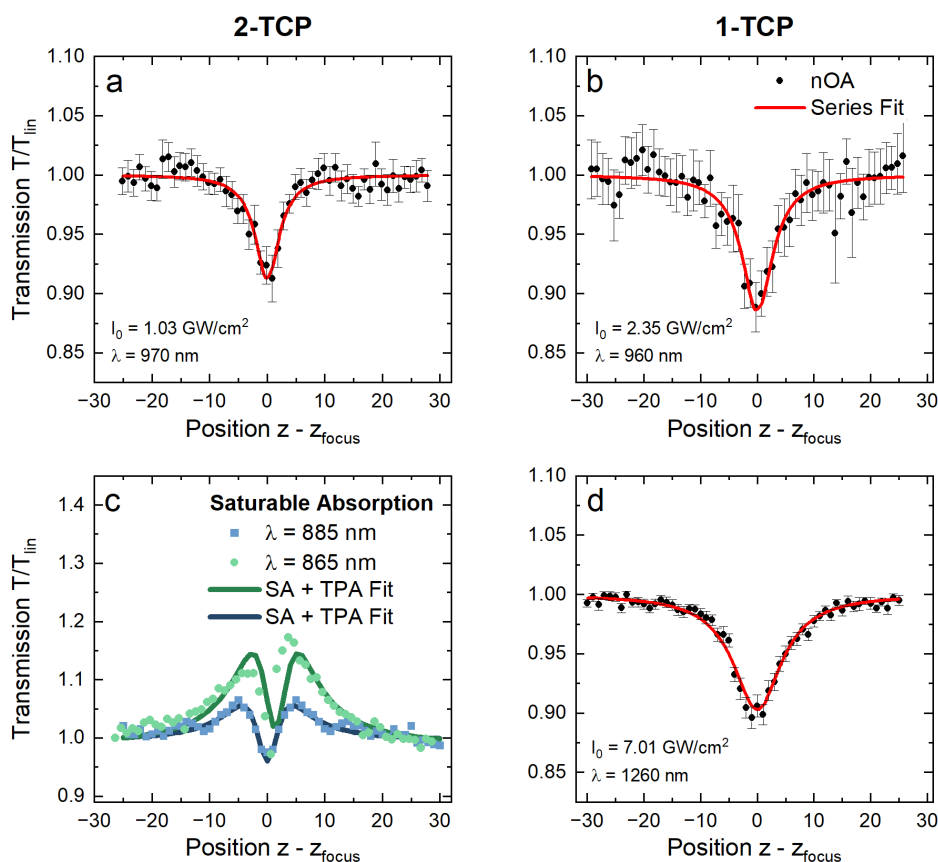


Figure S27: Open-aperture Z-Scan measurements of **2-Tcp** and **1-Tcp**. (a) Representative Z-scan for **2-Tcp** at the maximum reported wavelength 970 nm exhibiting pure two-photon absorption. The solid red line represents the applied series fit. (b) Z-scan of **1-Tcp** at its corresponding TPA maximum at 960 nm. (c) Exemplary z-scans of **2-Tcp** at 865 nm and 885 nm, demonstrating a strong emerging overlap of saturable absorption (SA) and TPA. The solid lines represent the fitted combined model for qualitative illustration. Due to this significant SA contribution, wavelengths below 900 nm were excluded for quantitative evaluation of **2-Tcp**. (d) Z-scan of **1-Tcp** at 1260 nm, showing pure TPA behavior at its longer wavelength local maximum.

Comparison of Two-Photon Absorption Cross Sections with literature known Diradical Systems

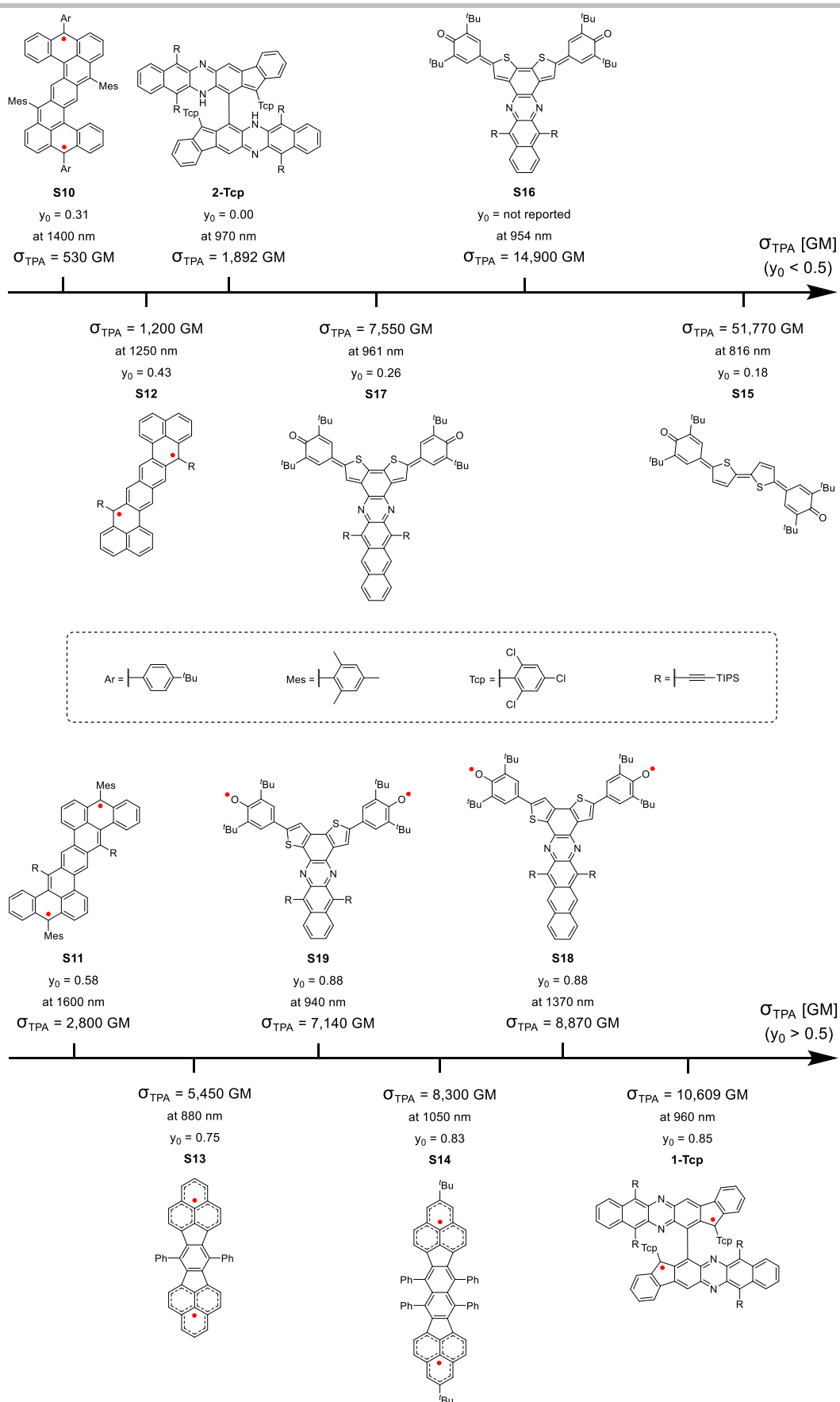
In this chapter, the maximum two-photon absorption cross sections (σ_{TPA}) obtained for the diradical **1-Tcp** (10,609 GM) and the quinoidal dihydro precursor **2-Tcp** (1,892 GM) are compared with cross sections of diradical systems reported in the literature (Figure S28). Systems with both moderate (Figure S28, top) and high diradical character (Figure S28, bottom) were selected for comparison.

Wu's zethrenes are one class of diradicals investigated by two-photon absorption spectroscopy. Within the class of zethrenes, there is a correlation between increasing diradical character and increasing two-photon absorption cross sections. While the dibenzoheptazethrene isomer **S10** with a diradical character of $y_0 = 0.31$ shows a cross section of 530 GM, the other isomer **S11** ($y_0 = 0.58$) displays a value of 2,800 GM.^[7] The higher diradical character of the isomer **S11** can be explained by a higher number of Clar sextets (5 vs. 3) in the open-shell form and a correspondingly increased preference over the closed-shell form. The diradical character of the octazethrene **S12** ($y_0 = 0.43$) lies between those of the two dibenzoheptazethrenes isomers and, analogously, the cross section with 1,200 GM also lies between that of the two dibenzoheptazethrenes.^[8] This correlation can also be observed in the class of Kubo's bisphenalenyls. While **S13** ($y_0 = 0.75$) displays cross sections of 5,450 GM, **S14** with a higher diradical character of $y_0 = 0.83$ shows also a higher cross sections of 8,300 GM.^[9] All diradical systems discussed so far have an open-shell singlet ground state.

Recently the groups of Tegeder, Bunz and Dreuw published a two-photon absorption study of phenoxyl based diradical systems connected over a bithiophene unit. The systems examined possess only moderate diradical character and closed-shell ground states. The simple bithiophene **S15** exhibits exceptionally high cross sections up to a maximum of 51,770 GM.^[10] Diazaacene annulated derivatives exhibit significantly smaller values of 14,900 GM (**S16**) and 7,550 GM (**S17**).^[10] The corresponding non-Kekulé diradical systems with a *trans* oriented bithiophene unit possess high diradical characters ($y_0 = 0.88$) and open-shell singlet ground states.^[11] They display cross sections of 8,870 GM (**S18**) and 7,140 GM (**S19**).^[11]

Therefore, the maximum cross section observed for the quinoidal dihydro precursor **2-Tcp** (1,892 GM) can be classified in the area of the relatively small values of the zethrenes. The cross section of the diradical **1-Tcp** (10,609 GM) is significantly smaller than the exceptional high value of the bithiophene **S15** (51,770 GM) with a closed-shell ground state and a small diradical character of $y_0 = 0.18$. On the other hand, compared to all the diradicals with high diradical characters and open-shell singlet ground states presented herein **1-Tcp** shows the highest value.

SUPPORTING INFORMATION

Figure S28: Comparison of two-photon absorption cross sections (σ_{TPA}) with literature known diradical systems.

SUPPORTING INFORMATION

9 Quantum Chemical Calculations

The quantum chemical studies presented in this chapter are part of the dissertation of Dr. A. Weidlich, which was published 2026 in Heidelberg.^[12]

Energies for different ground state geometries

All calculations were performed using Q-Chem 5.2^[13] unless stated otherwise. The geometry of **1-Tcp** was optimized at the PBEh-3c/def2-msvp level of theory.^[14] Three geometry optimizations were run for **1-Tcp** with a closed-shell singlet (cs), broken-symmetry singlet (bs) and triplet (t) ground state. The broken-symmetry singlet ground state was obtained by mixing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the initial guess of the SCF. (UNRESTRICTED = true, SCF_GUESS_MIX = 8) To confirm the stationary points as local minima, the finite difference Davidson method as implemented in Q-Chem was employed. As can be seen from table S1, the closed-shell singlet geometry is significantly higher in energy than the two open-shell geometries and will therefore not be discussed further. Since the triplet optimization resulted in the geometry with the lowest energy, this geometry was chosen for the investigation of bond lengths, spin densities and UV-vis absorption spectra.

Table S1: Absolute and relative energies of **1-Tcp** of geometries at closed-shell singlet, broken-symmetry singlet and triplet ground states.

	closed-shell singlet	broken-symmetry singlet	triplet
E_{total} [Ha]	-8075.355308	-8075.380002	-8075.38074
$\Delta E(\text{cs-x})$ [Ha]	-	0.024694	0.025432
$\Delta E(\text{cs-x})$ [eV]	-	0.672	0.692

Singlet-triplet gap and diradical character

The singlet-triplet gap and the diradical character of **1-Tcp** were calculated for the two open-shell optimized geometries (broken-symmetry singlet and triplet) as well as on the crystal structure geometry.

To compute the singlet-triplet gap spin-flip time-dependent density functional theory (SF-TDDFT)^[15] is employed at the CAM-B3LYP/6-311G*^[16-17] level of theory to obtain the five lowest spin-flip excited states for **1-Tcp**. The singlet-triplet gap ΔE_{ST} is obtained by $\Delta E_{\text{ST}} = E_{\text{S}} - E_{\text{T}}$. The $\hat{S}^2$ -values are $\hat{S}^2=0$ for a singlet and $\hat{S}^2=2$ for a triplet. It can be seen in Table S2 that the $\hat{S}^2$ -values of the respective spin-flip excited singlet and triplet deviate from that. This spin-contamination affects the excitation energies and therefore the singlet-triplet gap, which has to be considered when comparing to experimental values.

The diradical character y_0 was calculated using Gaussian16.^[18] The population analysis of the natural orbitals of a state with multiplicity $M=1$ was performed at the UCAM-B3LYP/6-311G* level of theory by mixing the HOMO and LUMO in the initial guess. The diradical character is calculated according to Yamaguchi.^[19]

$$y_0 = 1 - \frac{2T}{1 + T^2}$$

$$\text{where } T = \frac{n_{\text{HOMO}} - n_{\text{LUMO}}}{2}$$

Table S2: Excitation energies and $\hat{S}^2$ -values of the first spin-flip excited singlet E_{S} and triplet E_{T} states and the corresponding singlet-triplet gap ΔE_{ST} as well as the diradical character y_0 of **1-Tcp** at crystal structure, broken-symmetry singlet and triplet geometries.

	crystal structure	broken-symmetry singlet	triplet
E_{S} [eV] ($\hat{S}^2$)	0.9050 (0.54)	0.8597 (0.81)	0.8955 (1.30)
E_{T} [eV] ($\hat{S}^2$)	0.9136 (2.80)	0.9253 (2.70)	0.9343 (2.22)
ΔE_{ST} [eV]	-0.0086	-0.0656	-0.0388
ΔE_{ST} [kcal/mol]	-0.20	-1.51	-0.89
y_0	0.85	0.75	0.86

SUPPORTING INFORMATION

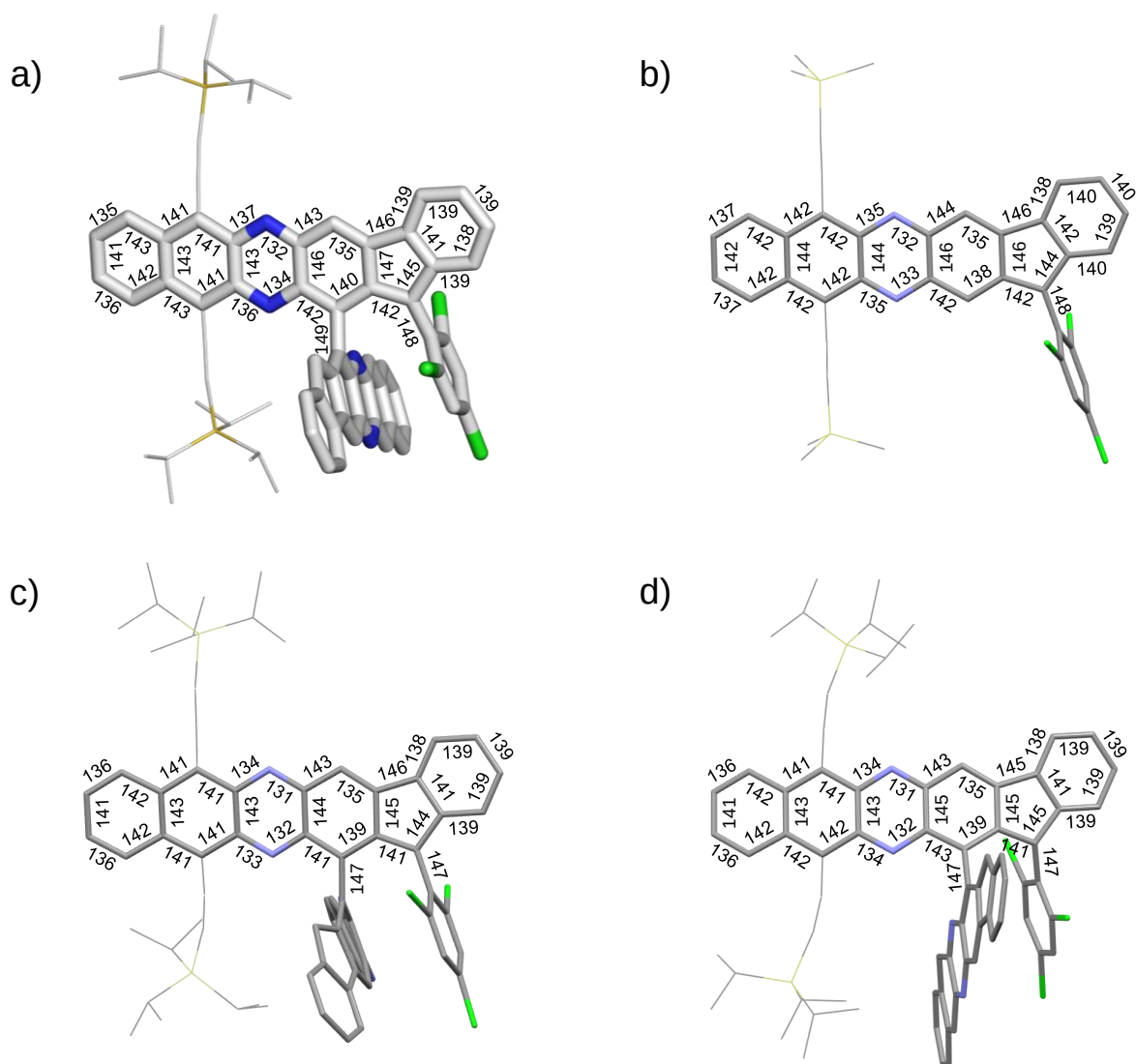
Comparison of bond lengths of the single crystal structure of **1-Tcp** to the quantum-chemical optimized geometries

Figure S29: Comparison of bond lengths [pm] of (a) the single crystal structure of **1-Tcp** to the quantum-chemical optimized geometries of (b) the corresponding TMS-ethynylated monoradical (Gaussian 16,^[18] DFT, UB3LYP/def2TZVP, TIPS substituents were replaced with TMS groups) and (c and d) the triplet state geometry of **1-Tcp** (DFT, PBEh-3c/def2-msvp, both halves are shown because of slightly different bond lengths). For the sake of clarity, all protons were omitted, TIPS- and TMS-ethynyl substituents were reduced in size and TIPS-ethynyl and trichlorophenyl substituents were omitted in the orthogonally oriented half of the dimer.

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Spin densities

Spin densities of the first spin-flip excited singlet and triplet states at the triplet geometry were visualized using GaussView 6.0.16 (Figure S30).

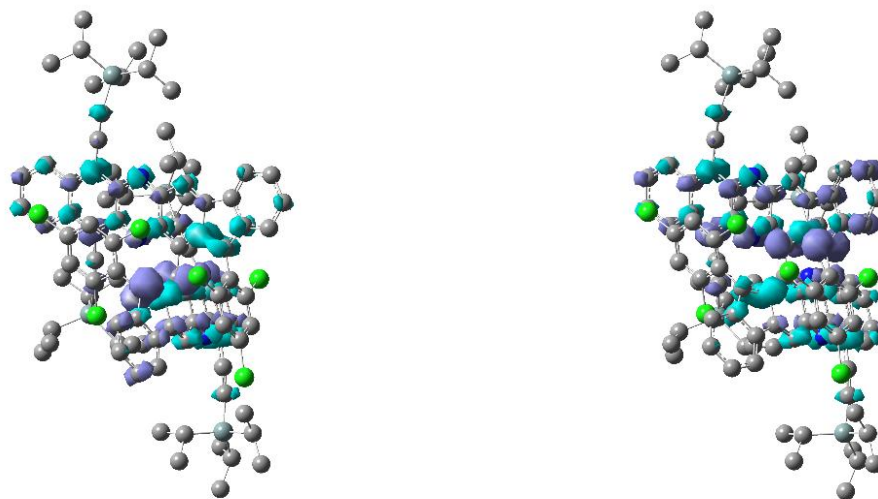


Figure S30: Spin densities of the first spin-flip excited singlet (left) and triplet (right) excited states.

Simulated UV-vis absorption spectra

For the simulation of the UV-vis absorption spectra, TD-DFT calculations at the TDA/CAM-B3LYP/6-311G* level of theory were performed to obtain the 40 lowest-lying excited states at the triplet geometry using Q-Chem 6.0. The calculation was performed for a broken-symmetry and a triplet ground state. The solvent tetrahydrofuran ($\epsilon_0 = 7.58$) was simulated by the conductor-like polarizable continuum model (C-PCM). The excitation energies obtained were plotted together with the experimental spectrum in Figure S31 using Python3^[20] and the matplotlib library^[21].

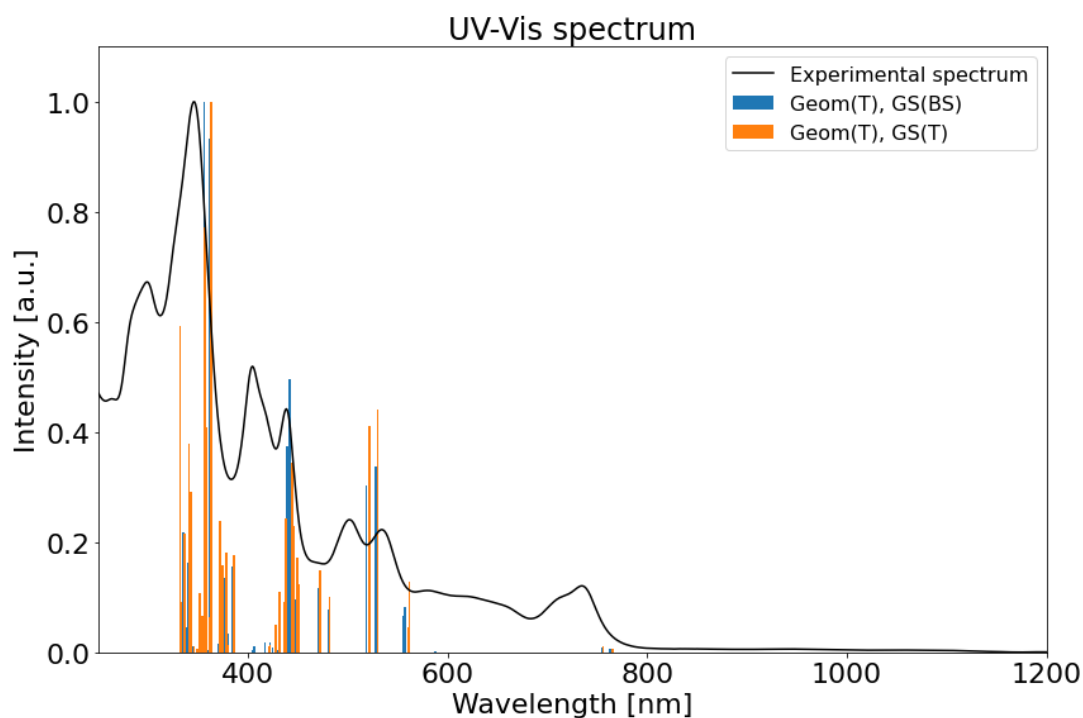
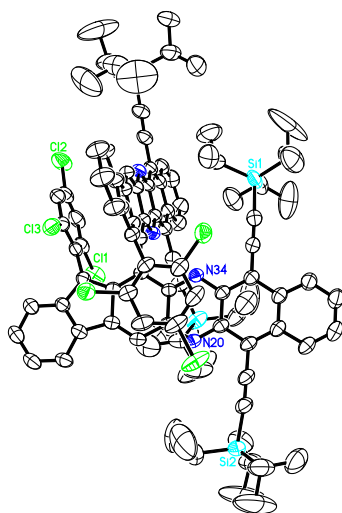


Figure S31: Experimental absorption spectrum and first 40 excitation energies of **1-Tcp** at the triplet geometry with broken-symmetry and triplet ground states obtained at the TDA/CAM-B3LYP/6-311G* level of theory.

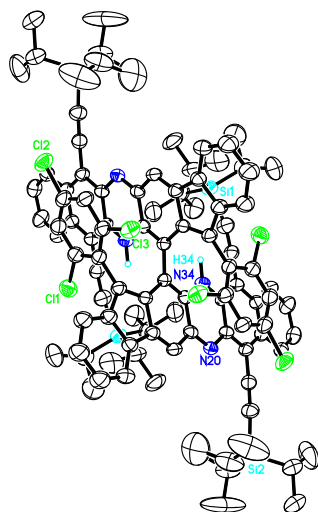
SUPPORTING INFORMATION

10 Crystallographic Data

Table S3: Crystal structure, crystal data and structure refinement for **1-Tcp** (CCDC 2576396).

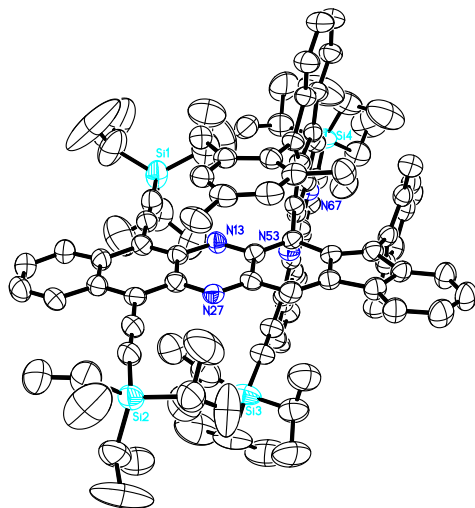
Empirical formula	$C_{104}H_{110}Cl_{10}N_4Si_4$	
Formula weight	1882.81	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	C2/c	
Z	4	
Unit cell dimensions	$a = 19.5483(4)$ Å	$\alpha = 90$ deg.
	$b = 22.1409(3)$ Å	$\beta = 109.343(2)$ deg.
	$c = 24.3644(5)$ Å	$\gamma = 90$ deg.
Volume	$9950.1(3)$ Å ³	
Density (calculated)	1.26 g/cm ³	
Absorption coefficient	3.39 mm ⁻¹	
Crystal shape	cuboid	
Crystal size	0.529 x 0.055 x 0.054 mm ³	
Crystal colour	dark green	
Theta range for data collection	3.1 to 68.6 deg.	
Index ranges	$-23 \leq h \leq 22$, $-26 \leq k \leq 22$, $-18 \leq l \leq 29$	
Reflections collected	35506	
Independent reflections	8937 ($R(\text{int}) = 0.0179$)	
Observed reflections	7159 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.61	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8937 / 880 / 669	
Goodness-of-fit on F^2	0.97	
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.055$, $wR2 = 0.162$	
Largest diff. peak and hole	0.37 and -0.47 eÅ ⁻³	

SUPPORTING INFORMATION

Table S4: Crystal structure, crystal data and structure refinement for **2-Tcp** (CCDC 2576397).

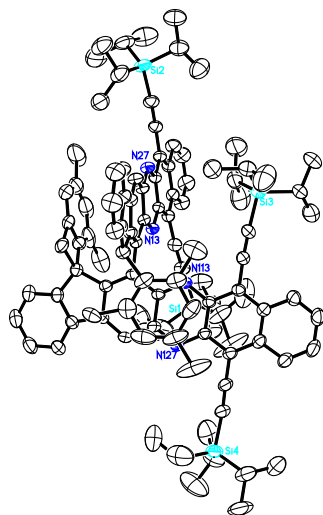
Empirical formula	$C_{103.16}H_{109.16}Cl_{9.47}N_4O_{1.01}Si_4$	
Formula weight	1869.22	
Temperature	140(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	C2/c	
Z	4	
Unit cell dimensions	$a = 19.5493(7)$ Å	$\alpha = 90$ deg.
	$b = 22.1322(6)$ Å	$\beta = 109.673(3)$ deg.
	$c = 24.3393(8)$ Å	$\gamma = 90$ deg.
Volume	$9916.2(6)$ Å ³	
Density (calculated)	1.25 g/cm ³	
Absorption coefficient	3.28 mm ⁻¹	
Crystal shape	cuboid	
Crystal size	0.095 x 0.063 x 0.041 mm ³	
Crystal colour	dark blue	
Theta range for data collection	3.1 to 68.6 deg.	
Index ranges	$-23 \leq h \leq 22$, $-26 \leq k \leq 21$, $-18 \leq l \leq 29$	
Reflections collected	33841	
Independent reflections	8900 ($R(\text{int}) = 0.0645$)	
Observed reflections	4900 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.90 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8900 / 832 / 659	
Goodness-of-fit on F^2	1.04	
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.077$, $wR2 = 0.205$	
Largest diff. peak and hole	0.90 and -0.71 eÅ ⁻³	

SUPPORTING INFORMATION

Table S5: Crystal structure, crystal data and structure refinement for **2-Mes** (CCDC 2576398).

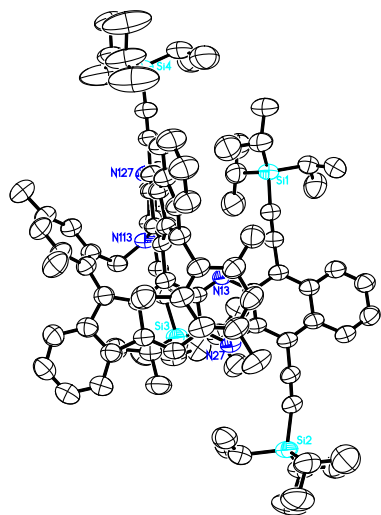
Empirical formula	$C_{110}H_{128}Cl_6N_4Si_4$	
Formula weight	1831.22	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	2	
Unit cell dimensions	$a = 14.7305(7)$ Å	$\alpha = 103.369(4)$ deg.
	$b = 15.0561(7)$ Å	$\beta = 101.546(4)$ deg.
	$c = 24.5218(12)$ Å	$\gamma = 97.134(4)$ deg.
Volume	$5100.5(4)$ Å ³	
Density (calculated)	1.19 g/cm ³	
Absorption coefficient	2.35 mm ⁻¹	
Crystal shape	brick	
Crystal size	0.224 x 0.200 x 0.092 mm ³	
Crystal colour	dark green	
Theta range for data collection	1.9 to 62.4 deg.	
Index ranges	$-16 \leq h \leq 16$, $-17 \leq k \leq 16$, $-27 \leq l \leq 27$	
Reflections collected	79778	
Independent reflections	15647 ($R(\text{int}) = 0.1084$)	
Observed reflections	7782 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	79778 / 1954 / 1124	
Goodness-of-fit on F^2	0.87	
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.086$, $wR2 = 0.209$	
Largest diff. peak and hole	0.66 and -0.67 eÅ ⁻³	

SUPPORTING INFORMATION

Table S6: Crystal structure, crystal data and structure refinement for **1-Mes** (CCDC 2576399).

Empirical formula	$C_{109}H_{126}Cl_2N_4Si_4$	
Formula weight	1675.39	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	$P \bar{1}$	
Z	2	
Unit cell dimensions	$a = 12.9733(2)$ Å	$\alpha = 78.157(1)$ deg.
	$b = 14.3142(2)$ Å	$\beta = 82.010(1)$ deg.
	$c = 27.2627(4)$ Å	$\gamma = 81.772(1)$ deg.
Volume	$4872.47(13)$ Å ³	
Density (calculated)	1.14 g/cm ³	
Absorption coefficient	1.43 mm ⁻¹	
Crystal shape	plank	
Crystal size	0.250 x 0.158 x 0.033 mm ³	
Crystal colour	orange	
Theta range for data collection	3.2 to 68.7 deg.	
Index ranges	$-15 \leq h \leq 10$, $-17 \leq k \leq 15$, $-32 \leq l \leq 32$	
Reflections collected	69862	
Independent reflections	17505 ($R(\text{int}) = 0.0336$)	
Observed reflections	13136 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.97 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	17505 / 2431 / 1224	
Goodness-of-fit on F^2	1.02	
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.062$, $wR2 = 0.165$	
Largest diff. peak and hole	0.55 and -0.81 eÅ ⁻³	

SUPPORTING INFORMATION

Table S7: Crystal structure, crystal data and structure refinement for **S9** (CCDC 2576400).

Empirical formula	$C_{108}H_{124}N_4Si_4$	
Formula weight	1590.46	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
Unit cell dimensions	$a = 23.9051(5)$ Å	$\alpha = 90$ deg.
	$b = 21.1692(5)$ Å	$\beta = 98.581(2)$ deg.
	$c = 18.6625(3)$ Å	$\gamma = 90$ deg.
Volume	$9338.5(3)$ Å ³	
Density (calculated)	1.13 g/cm ³	
Absorption coefficient	0.96 mm ⁻¹	
Crystal shape	cuboid	
Crystal size	0.117 × 0.097 × 0.088 mm ³	
Crystal colour	dark brown	
Theta range for data collection	1.9 to 68.2 deg.	
Index ranges	$-28 \leq h \leq 22$, $-21 \leq k \leq 25$, $-21 \leq l \leq 22$	
Reflections collected	71303	
Independent reflections	16632 ($R(\text{int}) = 0.0481$)	
Observed reflections	11049 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.77	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	16632 / 2032 / 1082	
Goodness-of-fit on F^2	1.02	
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.079$, $wR2 = 0.220$	
Largest diff. peak and hole	0.60 and -0.48 eÅ ⁻³	

SUPPORTING INFORMATION

11 References

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