Synthesis and Transport Studies of a Cofacial Porphyrin Cyclophane

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ABSTRACT: Porphyrin cyclophane 1, consisting of two rigidly fixed but still movable cofacial porphyrins and exposing acetate masked thiols in opposed directions of the macrocycle, is designed, synthesized, and characterized. The functional cyclophane 1, as pioneer of mechanosensitive 3D materials, forms stable single molecule junctions in a mechanically controlled break junction setup. Its reliable integration in a single molecule junction is a fundamental prerequisite to explore the potential of these structures as mechanically triggered functional units and devices.

INTRODUCTION

Molecular junction investigation, as the first step of fundamental structure–property relationship studies of single molecules integrated into electric circuits, is a crucial research field toward establishing possible future devices. The successful implementation of functional molecules into electronic circuits exposing functionalities such as rectification or switching by the application of an external stimulus that forces the molecules into one of two discrete conductance states has been reported. Resistance response upon conformational changes of a molecular junction by quantum interference while altering the electrode’s distances was reported for oligophenylethynylenes (OPEs) in a mechanically controlled break junction (MCBJ) and imidazole derivatives using the scanning tunnelling microscopy break junction technique. In these cases, the spatial arrangement of a pair of stacking \( \pi \) systems attached to opposed electrodes is manipulated with respect to each other in a bimolecular junction. Single molecule mechano manipulation in MCBJs was achieved resulting in alternating spin states by ligand field distortion and further indicated the compression and elongation of helically arranged \( \pi \) systems. As first model compounds, rigid rots comprising [2.2]para cyclophanes (PCPs) have been integrated in molecular junctions to investigate their mechanosensitivity. Indeed, the resistance of the springlike single molecule junction could be controlled by distance modulation mechanically, with oscillations as a function of the electrode distance of more than an order of magnitude in conductance. Quantum chemistry calculations indicated this phenomenon to arise from destructive quantum interference effects between the frontier orbitals of the modulated \( \pi \) systems.

Porphyrrins are key components in nature’s machinery to store energy via photosynthesis. Their well established synthesis as well as their rich and fine tuneable electrical and optical properties make them particularly appealing building blocks for the construction of molecular devices. Conductance features of porphyrin wires and tapes as well as different anchorings to the electrode’s surface have been studied. In our previous work, we showed that porphyrins form stable single molecule junctions in a MCBJ setup in which three different conductance pathways were distinguished using an unsupervised clustering algorithm. From a molecular design perspective, porphyrins have an additional appealing structural feature: They enable the perpendicular/right angled arrangement of functional subunits in their meso positions. This makes them ideal building blocks to construct a cyclophane that allows mechanical manipulation of two cofacial porphyrins into the electrode direction by the compensation of the physical stress over laterally attached bridging units. Mechanical manipulation of such a cofacial \( \pi–\pi \) structure because of a continuously adjustable stimulus is expected to yield a distinct conductance response, which possibly opens the door to a new class of mechano sensitive molecular electronic components, such as potentiometers. Inspired by the topology of PCPs and our previous findings, we desired to design, synthesize, and investigate porphyrin cyclophanes, suitable for mechanosensi
tive single molecule conductance experiments. Our first attempts toward mechanosensitive porphyrin cyclophanes were based on integrating a pair of porphyrin subunits into an OPE macrocycle. While our synthetic strategy did not yield the desired structure, yet the isolated threefold interlinked porphyrin dimer indicated the suitability of MCBJ experiments to study complex multilevel porphyrin architectures. 26

In this work, we report the synthesis and characterization of zinc(II) porphyrin cyclophanes 1 with its structural isomer 2, having the thioacetates in the same direction of the macrocycle. Additionally, we test the suitability of this new family of cyclophanes in MCBJ experiments with 1.

■ RESULTS AND DISCUSSION

Design. The cofacial porphyrin cyclophane 1 is decorated with one acetal masked thiol gold anchoring group per porphyrin subunit, pointing into opposed directions of the macrocycle as shown in Figure 1. Planar xanthene units bridge the macrocycle in the lateral positions of the porphyrins with respect to the anchoring groups. This ensures rigidity of the macrocyclic structure, while acetylenes between the bridge and the porphyrins provide revolving joints. The combination of rigid building blocks with revolving joints promises a controlled variation of the cofacial porphyrin arrangement upon mechanical manipulation of the electrode spacing.

When the structure is implemented into a molecular junction, distance modulation of the electrodes can be depicted as pulling and pushing on the anchoring groups of the macrocycle. Increasing and decreasing the distance of the electrodes should thus be compensated by a translational movement of the porphyrin planes with respect to each other. At the same time, the spacing between the two porphyrin planes should be altered. While detailed insights into the mechanisms of such conformational responses to the distance modulation will require in depth analysis and theoretical studies, the working principle of the mechano sensitive conformational response of the target structure 1 is outlined in Figure 2. As a guide for the eye, the distances of the two porphyrins between each other upon manipulating the electrode distance are visualized by arrows.

Retrosynthesis. The retrosynthetic plan toward 1 is displayed in Scheme 1. In a first step, the thioacetate functional groups were planned to be trans protected from their tert butyl analogues, which are suitably stable regarding the conditions required for the overall synthesis. The formation of the macrocyclic structure was expected to be accessible by a palladium mediated fourfold Sonogashira–Hagihara cross coupling reaction of two molecules of 3 and two molecules of 2,7 di tert butyl 4,5 diiodo 9,9 dimethyl 9H xanthene 27 (4) under high dilution conditions. The highly functionalized porphyrin monomer 3 exposing both acetylenes for the macrocyclization after liberation of the tri iso propyl (TIPS) protecting groups and a single thio decorated phenyl acetylene was divided into single brominated zinc complex 5 and tert butyl (4 ethynylphenyl)sulfane 28 by means of Sonogashira–Hagihara cross coupling. Statistic bromination and metalation of 5,15 bis((tri iso propylsilyl)ethyl)porphyrin 29 (6) should provide 5.

Synthesis and Characterization. The synthetic overview is given in Scheme 2; detailed analytical data can be found in the Supporting Information.

In contrast to the meso bromination of arylporphyrins by N bromosuccinimide (NBS), the 10,20 meso di bromination of 5,15 meso acetylene decorated porphyrins are known to need a central magnesium(II) ion incorporated into the tetra dentate ligand in order to increase the electron density in the meso positions. 30 We found a suitable pseudo one pot, three step procedure for the statistical monobromination of 6 yielding 7 in 44% while recovering 33% of 6 involving one single silica gel column during isolation.

Treatment of a solution of 6 in CH2Cl2 with di iso propylethylamine (NPr2Et) and magnesium(II) iodide (MgI2) at room temperature (rt) provided the magnesium complex of 6 quantitatively within an hour (h) as indicated by thin layer chromatography (TLC) monitoring of the reaction. After aqueous workup, the crude product was subjected to bromination conditions using 1.1 equiv of NBS in a chloroform/pyridine solution. After 16 h of stirring at rt in the absence of light, the mixture was washed with water, and the separated organic phase was treated with trifluoroacetic acid (TFA) and stirred for 2 h at rt. After aqueous workup, the crude material was subjected to silica gel column chromatography (toluene 1:4 cyclohexane) where the desired monobrominated product 7 was isolated as the second eluting purple band besides the substrate 6 being the third eluting band. Treatment of a solution of 7 in CH2Cl2/CH3OH with an excess of zinc(II) acetate [Zn(OAc)2] afforded 5 quantitatively within 2 h at rt. Subsequent Sonogashira–Hagihara cross coupling of 5 and tert butyl (4

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Figure 1. Chemical structure of the target compound 1.

![Chemical structure of the target compound 1.](image1)

Figure 2. Proposed working principle of the laterally interlocked, mechano sensitive porphyrin cyclophane 1.

![Proposed working principle of the laterally interlocked, mechano sensitive porphyrin cyclophane 1.](image2)
ethynylphenyl)sulfane at elevated temperatures of 50 °C mediated by palladium(0) tetrakis(triphenylphosphine) \([\text{Pd}(\text{PPh}_3)_4]\) and copper(I) iodide \((\text{CuI})\) in degassed tetrahydrofuran (THF) and triethylamine \((\text{NEt}_3)\) afforded analytically...
pure 3 by reprecipitation of the crude reaction mixture from CH2Cl2/CH3OH after filtration over a short silica plug eluted with CH2Cl2 in good yields of 83%.

A one to one mixture of 3 and 4 in wet THF, thoroughly degassed by purging with argon, was treated with excess tetra n butyl ammonium fluoride (TBAF) to liberate the TIPS protected acetylenes of 3. Once the reaction was completed as indicated by TLC, the mixture was cannula transferred into a previously degassed solution of THF and NEt3 containing Pd(PPh3)4 and CuI. The resulting 1 M solution of deprotected 3 and 4 was sealed under argon and placed in a preheated oil bath at 80 °C where it was vigorously stirred for 16 h. The mixture was evaporated to dryness, and the residue was subjected to silica gel column chromatography (CH2Cl2 1:1 cyclohexane). The eluted purple fraction comprising molecules with the expected masses of the target macrocycle as well as open chain oligomers [determined by matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI ToF MS)] was collected, concentrated, and subjected to automated recycling gel permeation chromatography (GPC) in chloroform. The slowest running and the second slowest running bands showing typical UV−vis traces for porphyrins were collected and evaporated to dryness. Both compounds were found to have the same mass by means of high resolution electrospray ionization time of flight mass spectrometry (HR ESI ToF MS), fitting the molecular composition of macrocycles 8 and 9. The observed difference in hydrodynamic radii while performing GPC led to the conclusion that the slowest eluting band should be the geminally interlocked porphyrin cyclophane 9, while the band showing a slightly increased hydrodynamic radius was proposed to be target 5, pseudo 15 functionalized porphyrin cyclophane 8. Macrocycles 8 and 9 were isolated in yields of 5.4 and 4.2%, respectively. The expected signals of the macrocyclic structures were observed in the proton nuclear magnetic resonance (1H NMR) spectrum of the individual samples, with distinct differences in the chemical shifts of the signals but not in their number and multiplicities. Four low field aromatic \(^3J\) doublets corresponding to the \(\beta\) protons (3, 4, 7, and 8 in Figure 3), one single singlet for the meso proton (9 in Figure 3), two aromatic \(^3J\) doublets of the xanthene bridge (5 and 6 in Figure 3), and an aromatic AB system arising from the anchoring group bearing phenyl (1 and 2 in Figure 3) were observed in the aromatic region, as assigned by two dimensional 

\(^1H−^1H\) nuclear Overhauser enhancement spectroscopy (Figures S25, S26, S34, and S35).

The UV−vis spectrum of the samples showed a symmetric Soret band, typical for rigidly bridged porphyrin cyclophanes.\(^{31}\) The absence of exciton coupling between the two porphyrins indicated parallelism of the π−π system in solution. The Soret bands of the macrocyclic structures 8 \([\lambda_{Soret} = 442\text{ nm}, \log(\varepsilon) = 5.56]\) and 9 \([\lambda_{Soret} = 437\text{ nm}, \log(\varepsilon) = 5.62]\) were found to be blue shifted in comparison to the monomer 3 \([\lambda_{Soret} = 447\text{ nm}, \log(\varepsilon) = 5.61]\), while the Q bands of 8 \([\lambda_{Q1} = 595\text{ nm}, \log(\varepsilon) = 4.10\text{ and } \lambda_{Q2} = 645\text{ nm}, \log(\varepsilon) = 4.52]\) and 9 \([\lambda_{Q1} = 593\text{ nm}, \log(\varepsilon) = 4.20\text{ and } \lambda_{Q2} = 642\text{ nm}, \log(\varepsilon) = 4.58]\) appeared red shifted compared to 3 \([\lambda_{Q1} = 581\text{ nm}, \log(\varepsilon) = 4.45\text{ and } \lambda_{Q2} = 627\text{ nm}, \log(\varepsilon) = 4.31]\) as shown in Figure 4.

![Figure 3](image-url)  
<Figure 3. Stacked aromatic region of the \(^1H\) NMR spectra of (a) 8 and (b) 9 recorded in THF \(_d_6\) at 298 K operating on a 500 MHz proton frequency. (c) Symmetry reduced and labelled structures of 8 and 9.>

![Figure 4](image-url)  
<Figure 4. Normalized UV−vis spectra of 3 (black), 8 (red), and 9 (blue) recorded in CH2Cl2. Changes from monomer to cyclophane are visualized by black arrows.>

Single crystals suitable for X ray analysis were obtained by top layering a THF solution of 8 and 9 with methanol (see Figure 5). Extracted from these solid state structures, the porphyrin to porphyrin plane distance of 8 was determined to be 3.24 Å, thus 0.16 Å smaller than the carbon to carbon van der Waals distance. The thiol to thiol distance of the target 5, pseudo 15 functionalized porphyrin cyclophane 8, was extracted...
to be 20.5 Å. The geminally interlocked porphyrin cyclophane 9, on the other hand, showed an increased plane to plane distance of 3.45 Å and a short thiol to thiol distance of 5.06 Å, compared to 8, in the solid state structure.

Both of these isomers (8 and 9) were subjected to trans protection conditions in order to make the structures suitable to contact noble metal surfaces via in situ deprotection of the thioacetates upon formation of a covalent S–Au bond. 8 and 9 were each dissolved in dry and degassed toluene/acetonitrile and 175 equiv acetyl chloride (AcCl) in separate flasks under an argon atmosphere. The mixtures were treated with 3 equiv of bismuth(III) trifluoromethanesulphonate [Bi(OSO₂CF₃)₃] and stirred for 12 h at ambient temperature. TLC monitoring confirmed the completion of the reactions, and MALDI ToF MS analysis of the crude reaction mixtures revealed that besides trans protection of the tert butyl thioethers to thioacetates, demetalation took place, and the free base porphyrin cyclophanes 10 and 11 were isolated in moderate yields of 36 and 45%, respectively, by automated recycling GPC in chloroform. Treatment of these compounds in a CH₂Cl₂/CH₃OH solution with excess Zn(OAc)₂ showed slow but clean conversion of free base cyclophanes 10 and 11 to zinc complexes 1 and 2 in excellent yields of 96 and 89% after 1 day, respectively.

Having these four thioacetate functionalized cofacial porphyrin cyclophanes (1, 2, 10, and 11) suitable for gold electrode contacting in hands, we desired to test the suitability of 1 toward single molecule conductance experiments, as discussed in the following section.

**Single-Molecule Conductance Measurements.** The herein reported porphyrin cyclophane 1 was designed to absorb distance variations of an electrode pair in a molecular junction by altering the arrangement of both cofacial porphyrin subunits. The dimension of the structure and even more its division into two spatially separated porphyrin subunits raised concerns with respect to its suitability for single molecule junctions. To investigate single molecule junctions comprising the cofacial porphyrin cyclophane 1, the compound was integrated in an electronic circuit using a MCBJ setup. The MCBJ technique is particularly appealing to investigate the mechanical properties and stability of single molecule junctions since the

**Figure 5.** Oak Ridge thermal ellipsoid plot representation of the solid state structure of (a) 8 and (b) 9. Thermal ellipsoids are plotted on a 50% probability level. Solvent molecules, solubilizing groups, and hydrogen atoms are omitted for clarity. Red arrows indicate the plane to plane distances; blue arrows indicate the thiol to thiol distances.

**Figure 6.** (a) Two dimensional conductance displacement histogram built from 5113 consecutive breaking traces. The measurement is performed after the deposition of a 5 μM dichloromethane solution containing 1. The applied bias is 100 mV, and the electrode speed is 2.5 nm/s. (b) Tunnelling and (c) molecular breaking traces separated from (a) by the clustering method shown in ref 36 with two classes. The yield of the molecular traces obtained from the clustering method is approximately 4%.
To verify that in both fast and self breaking experiments, comparable molecules were trapped inside the gap between both electrodes, one dimensional (1D) conductance histograms of the molecular junctions for both methods were constructed; they are displayed in Figure 7. The 1D histogram of the 4% molecular junctions spotted in the fast breaking experiment (Figure 7a) reveals a conductance peak with a maximum located at $4.1 \times 10^{-6} \text{G}_0$ and a spread of about 2 orders of magnitude in conductance. With the self breaking technique, the 1D histogram features a single conductance peak, representing the most relaxed molecular junction configuration with its maximum at $6.8 \times 10^{-6} \text{G}_0$ (Figure 7b). The good agreement between both 1D histograms corroborates the reliable and repetitive formation of comparable single molecule junctions with the here reported porphyrin cyclophane I. This result and the evolution of the conductance with length in the two dimensional histograms support the intended arrangement of the molecule being immobilized by each thiol anchor group to one of both opposed electrodes of the MCBJ.

The here reported MCBJ experiments with porphyrin cyclophane I not only demonstrate the suitability of this mechanically adaptive molecular structure for electronic transport experiments but also already display individual molecular traces with conductance oscillations pointing at the mechanosensitivity of the structure. However, the in-depth analysis of the electro mechanical behavior requires not only extensive additional transport experiments and their analyses but also theoretical support, simulating how the molecules respond to mechanical stress and investigating the corresponding impact on the electronic transparency of the junction. Our current activities are geared in this direction.

**CONCLUSIONS**

Based on the experience of our previous reports, we designed the rigidly interlocked cofacial porphyrin cyclophane I bearing one
thioacetate group per porphyrin subunit to anchor noble metal surfaces. Both the desired 5, pseudo 15, and the geminal thio functionalized derivatives of the macrocycle, protected with tert butyl groups, were synthesized and characterized by NMR and UV–vis spectroscopies, MS, and X ray analysis. Last step trans protection to the thioacetates enabled covalent S–Au bond formation in our MCBJ setup. Single molecule electronic transport experiments of the target compound I revealed well behaving and suitably stable single molecule junctions of this multilevel porphyrin architecture. Specifically, the fast breaking experiments indicated well defined conductance features in the range from $10^{-5}$ to $10^{-6} G_0$ with some traces showing conductance oscillations of up to an order of magnitude while stretching the junctions. On the other hand, the self breaking conductance oscillations of up to an order of magnitude while stretching the junctions. On the other hand, the self breaking conductance oscillations of up to an order of magnitude while stretching the junctions. On the other hand, the self breaking conductance oscillations of up to an order of magnitude while stretching the junctions. On the other hand, the self breaking conductance oscillations of up to an order of magnitude while stretching the junctions. On the other hand, the self breaking conductance oscillations of up to an order of magnitude while stretching the junctions.

### EXPERIMENTAL PART

**General Remarks.** Reagents and Solvents. All commercially available compounds were purchased from Sigma Aldrich, Acros, Apollo Scientific, Alfa Aesar, and Fluorochem and used without further purification. Column chromatography was performed on silica gel 60 (40–63 μm) from SilicylincTM, and the solvents were as technical grade. TLC was performed with silica gel 60 F254 glass plates purchased from Merck.

**Analytics and Instruments.** NMR experiments were performed on Bruker Avance III NMR spectrometers operating at 250, 400, or 500 MHz proton frequencies. The instruments were equipped with a direct observe 5 mm BBFO smart probe (250, 400 MHz) or an indirect 500 MHz proton frequencies. The instruments were equipped with a direct observe 5 mm BBFO smart probe (250, 400 MHz) or an indirect 500 MHz proton frequencies. The instruments were equipped with a direct observe 5 mm BBFO smart probe (250, 400 MHz) or an indirect 500 MHz proton frequencies.

**Preparation of 5.** A solution of 3 (tri iso propylsilyl)propionaldehyde (4.14 mL, 16.8 mmol, 1.0 equiv) and di(1H pyrrol 2 yl)methane (2.46 g, 16.8 mmol, 1.0 equiv) in CH2Cl2 (1.0 L) was purged with argon for 20 min at rt. Borontrifluoride etherate (0.68 mL, 5.54 mmol, 0.3 equiv) was added, and the reaction mixture was stirred for 45 min at rt. 2,3 Dichloro 5,6 dicyano 1,4 benzonitrile (5.72 g, 25.2 mmol, 1.5 equiv) was added, and the mixture was stirred for 1 h at rt. The reaction mixture was filtered over a plug of silica eluted with CH2Cl2 and concentrated under reduced pressure. Reprecipitation from CH2Cl2/CH3OH gave the title compound 6 (1.56 g, 2.33 mmol, 28%) as a microcrystalline purple solid. mp >300 °C; H NMR (500 MHz, CDCl3, 298 K, δ/ppm): 10.11 (s, 2H, Hmeso), 9.71 (d, $J_{HH} = 4.5$ Hz, 4H, H$_3$), 9.29 (d, $J_{HH} = 4.5$ Hz, 4H, H$_3$), 1.50–1.46 (m, 42H, H$_{TIPS}$), –2.71 (s, 2H, CH$_2$). $^1{C}$H (126 MHz, THF, $d_8$ 298 K, δ/ppm): 133.3, 130.9, 109.4, 108.1, 100.5, 99.9, 19.7, 13.0. Not all carbon atoms are visible due to π stacking and the quadrupolar momentum of the nitrogen atoms. HRMS (ESI +): m/z calc for C$_{42}$H$_{54}$BrN$_4$Si$_2$ [M + H$^+$], 787.3208; found, 787.3198. UV/VIS (CH$_2$Cl$_2$): $\lambda_{max}$ [nm] = 416, 492, 524, 640, 656.

**10-Bromo-5,15-bis[(tri iso propylsilyl)ethynyl]porphyrin (7).** Mgl$_2$ (601 mg, 2.16 mmol, 2.0 equiv) was added to a degassed solution of 6 (752 mg, 1.08 mmol, 1.0 equiv) in CH$_2$Cl$_2$/PyCNMe (250 mL, 100:1), and the resulting mixture was stirred at rt for 1 h while the purple solution turned dark green. The solution was washed with water three times, and the combined aqueous phase was extracted with CH$_2$Cl$_2$ twice. The combined organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was redissolved in CHCl$_3$ (0.5 L) and pyridine (5.0 mL). NBS (221 mg, 1.19 mmol, 1.1 equiv) was added, and the reaction mixture was stirred for 16 h at rt in the absence of light. The solution was washed with water three times, and the combined aqueous phase was extracted with CH$_2$Cl$_2$ twice. The combined organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure, and redissolved in CH$_2$Cl$_2$ (200 mL). TFA (0.40 mL, 5.40 mmol, 50 equiv) was added, and the resulting mixture was stirred at rt for 2 h while the green solution turned dark purple. The solution was washed with water three times, and the combined aqueous phase was extracted with CH$_2$Cl$_2$ twice. The combined organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure.

**General Remarks.** Reagents and Solvents. All commercially available compounds were purchased from Sigma Aldrich, Acros, Apollo Scientific, Alfa Aesar, and Fluorochem and used without further purification. Column chromatography was performed on silica gel 60 (40–63 μm) from SilicylincTM, and the solvents were as technical grade. TLC was performed with silica gel 60 F254 glass plates purchased from Merck.
The residue was reprinified from CH2Cl2/CH3OH yielding 3 (211 mg, 229 μmol, 83%) as a microcrystalline purple solid. mp >300°C. 1H NMR (500 MHz, THF-d8, 298 K, δ/ppm): 9.12 (d, JHH = 4.3 Hz, 4H, HXant), 8.86 (d, JHH = 4.4 Hz, 4H, HXant), 8.08 (s, 2H, Hmeso), 8.04 (d, JHH = 2.3 Hz, 4H, Hmeso), 7.94−7.98 (m, 4H, Hmeso), 7.94−7.98 (d, JHH = 2.3 Hz, 4H, HXant), 7.77−7.71 (m, 4H, Hmeso), 2.03 (s, 12H, HMe), 1.58 (s, 36H, HMe), 1.42 (s, 18H, HMe). 13C{1H} NMR (126 MHz, THF-d8, 298 K, δ/ppm): 192.9, 150.8, 147.1, 135.8, 133.3, 131.2, 130.6, 130.1, 129.7, 127.9, 126.4, 126.3, 125.3, 112.8, 108.5, 104.2, 101.8, 99.1, 95.6, 95.6, 94.0, 93.7, 55.0, 36.5, 35.7, 33.3, 32.1, 30.8, 30.4. Not all carbon atoms are visible due to π stacking and the quadrupolar momentum of the nitrogen atoms. HRMS (ESI, +): m/z calc for C120H103N8O4S2Zn2 [M + H]+, 1701.676; found, 1701.6728. UV/VIS (CH3Cl): λmax [nm] = 434, 621, 711.

1: A solution of 10 (1.98 mg, 1.16 μmol, 1.0 equiv) and Zn(OAc)2 (10.6 mg, 58.1 μmol, 50 equiv) in CH2Cl2 (5.0 mL) and CH3OH (5.0 mL) was stirred for 1 d at rt when TLC monitoring indicated completion [SiO2 CH3Cl/cyclohexane (2:1)]. The mixture was poured into water and extracted with CH2Cl2, dried over anhydrous Na2SO4, and concentrated under reduced pressure. One run over a size exclusion column (Bio Beads SX1 in toluene) gave the title compound 1 (2.03 mg, 1.11 μmol) as an amorphous solid in 96% yield. 1H NMR (500 MHz, THF-d8, 298 K, δ/ppm): 9.61 (d, JHH = 4.2 Hz, 4H, HXant), 9.42 (d, JHH = 4.3 Hz, 4H, HXant), 8.48 (s, 2H, Hmeso), 8.44 (d, JHH = 4.3 Hz, 4H, HXant), 8.09 (d, JHH = 2.3 Hz, 4H, HXant), 8.01 (d, JHH = 4.3 Hz, 4H, Hmeso), 7.94−7.89 (m, 4H, Hmeso), 7.85−7.81 (m, 8H, HXant + Hmeso), 2.61 (s, 6H, Hmeso), 2.03 (s, 12H, HMe), 1.59 (s, 36H, HMe). No 13C{1H} NMR spectrum was recorded due to poor solubility and little amounts of the compound. HRMS (ESI, +): m/z calc for C114H92N8O4S2Zn [M + CH3CO2]−, 1883.5991; found, 1883.5120. UV/VIS (CH3Cl): λmax [nm] = 445, 605, 653.

11: To a solution of 9 (15 mg, 8.08 μmol) and acetyl chloride (0.10 mL, 1.41 mmol, 175 equiv) in dry and degassed toluene (4.0 mL) and acetonitrile (4.0 mL) was added bismuth(III) trifluoromethanesulfonate (15.9 mg, 24.2 μmol, 3.0 equiv). The reaction mixture was stirred at rt for 16 h when TLC monitoring showed completion [SiO2 CH2Cl2/cyclohexane (2:1)]. The mixture was poured into water and extracted with toluene. The combined organic phase was dried over anhydrous Na2SO4. The crude was concentrated, redissolved in CH3Cl2, and subjected to automated GPC yielding 11 (7.5 mg, 4.48 μmol) as an amorphous solid in 55% yield. 1H NMR (500 MHz, THF-d8, 298 K, δ/ppm): 9.45 (d, JHH = 4.5 Hz, 4H, HXant), 9.37 (d, JHH = 4.4 Hz, 4H, Hmeso), 9.09 (d, JHH = 4.5 Hz, 4H, Hmeso), 8.62 (s, 2H, Hmeso), 8.48 (d, JHH = 4.4 Hz, 4H, Hmeso), 8.10−8.07 (m, 4H, Hmeso), 8.01 (d, JHH = 2.3 Hz, 4H, HXant), 7.87 (d, JHH = 2.3 Hz, 4H, HXant), 7.67−7.63 (m, 36H, Hmeso), 2.54 (s, 6H, Hmeso), 2.05 (s, 6H, Hmeso), 2.04 (s, 6H, Hmeso), 1.56 (s, 36H, Hmeso) −5.72 (s, 4H, HXant). 13C{1H} NMR (126 MHz, THF-d8, 298 K, δ/ppm): 192.8, 150.9, 147.2, 135.6, 133.2, 131.2, 130.1, 129.5, 126.2, 125.2, 113.3, 107.2, 101.4, 100.3, 97.1, 96.5, 94.4, 93.8, 55.0, 36.3, 35.7, 32.1, 30.8. HRMS (ESI, +): m/z calc for C114H92N8O4S2Zn [M + CH3CO2]−, 1700.667; found, 1700.6646. UV/VIS (CH3Cl): λmax [nm] = 434, 617, 707.

2: A solution of 11 (2 mg, 1.17 μmol, 1.0 equiv) and Zn(OAc)2 (10.7 mg, 58.5 μmol, 50 equiv) in CH2Cl2 (5.0 mL) and CH3OH (5.0 mL) was stirred for 1 d at rt when TLC monitoring indicated completion
The mixture was washed with water and extracted with CH$_2$Cl$_2$ dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. One run over a size exclusion column (Bio Beads SX1 in toluene) gave the title compound 2 (1.9 mg, 1.04 μmol) as an amorphous solid in 89% yield. $^1$H NMR (500 MHz, THF $d_8$, 298 K, δ/ppm): 5.52 (d, $^1$J$_{HH}$ = 4.3 Hz, 4H, H$_2$), 9.46 (d, $^1$J$_{HH}$ = 4.2 Hz, 4H, H$_2$), 8.72 (d, $^1$J$_{HH}$ = 4.3 Hz, 4H, H$_2$), 8.11 (d, $^1$J$_{HH}$ = 4.2 Hz, 4H, H$_2$), 8.10 (d, 3H, H$_{Me}$), 1.58 (s, 36H, H$_2$), 1.04 (m, 4H, H$_{Ph}$), 7.85 (d, 4H, H$_{meso}$), 8.05 (d, 4H, H$_{Xant}$), 131.6, 131.4, 131.3, 131.2, 130.4, 129.7, 129.3, 126.7, 124.7, 113.9, 9.46 (d, 3H, H$_{meso}$), 8.72 (d, 3H, H$_{meso}$), 9.46 (d, 3H, H$_{meso}$), 192.9, 152.0, 151.5, 151.0, 150.5, 148.4, 147.0, 135.4, 133.0, 131.6, 131.4, 131.3, 131.2, 129.7, 129.3, 126.7, 124.7, 113.9, 107.2, 102.9, 98.0, 95.5, 95.2, 92.5, 36.3, 35.6, 33.4, 33.3, 32.1, 30.8. HRMS (ESI, +): m/z calcd for C$_{114}$H$_{88}$N$_8$O$_4$S$_2$Zn$_2$ [M]+, λ$_{max}$ [nm] = 441, 601, 648.

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