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Incorporation of the 1,5-Naphthalene Subunit into Heteroporphyrin Structure: Toward Helical Aceneporphyrinoids

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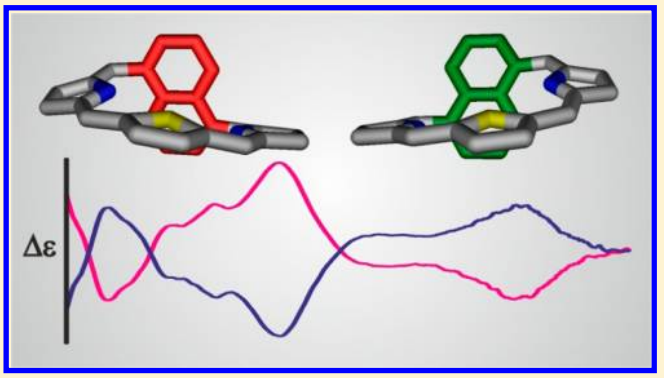
Supporting Information

ABSTRACT: 5,10,15,20-Tetraaryl-22-hetero-1,5-naphthiporphyrins, which contain a 1,5-naphthylene moiety instead of one pyrrole embedded in the macrocyclic framework of heteroporphyrins, were obtained by the [3 + 1] approach using the 1,5-naphthylene analogue of tripyrrane (1,5-bis(phenyl(2-pyrolyl)methyl)naphthalene) and 2,5-bis(arylhydroxymethyl)-heterocyclopentadiene (heterocyclopentadiene: thiophene, selenophene, tellurophene). The steric constraints, imposed by the substitution mode of the 1,5-naphthylene building block, resulted in the specific helical conformation of 22-hetero-1,5-naphthiporphyrins. The spectroscopic and structural properties of these aceneporphyrinoids indicate a lack of macrocycle aromaticity. Their protonation yielded solely dicationic species.



Aceneporphyrinoids combine structural features of polycyclic aromatic hydrocarbons and polypyrrolic macrocycles. A formal concept leading to higher aceneporphyrins(1.1.1.1) is based on an iterative approach involving addition of benzene units to a prearranged precursor molecule (Scheme 1). Thus, they are derived from benziporphyrins by applying a fusion of external benzene ring(s) and a built-in phenylene moiety, conserving the fundamental motive of parent *m*-benziporphyrin or *p*-benziporphyrin.

Such hybrid compounds exemplified by *m*-benziporphyrin,[1,2] *p*-benziporphyrin,[3] oxybenziporphyrins,[4,5] 24-thia-*p*-benziporphyrin,[6] 1,4-naphthiporphyrin,[7,8] 24-thia-1,4-naphthiporphyrin,[7] 1,3-naphthiporphyrin,[8] and its aromatic derivative 1,3-oxynaphthiporphyrin[9] create a unique macrocyclic environment toward coordination.[10,11] These molecules force atypical intermolecular reactivity,[7,12,13] for instance, a contraction of *p*-phenylene to cyclopentadiene that is triggered by insertion of palladium(II) into *p*-benziporphyrin.[12] In more general terms, aceneporphyrinoids are expected to reveal a broad spectrum of fundamentally important molecular properties among which are unexpected optical effects, electron transfer, and redox chemistry or three-dimensional aromaticity.

In principle, a variety of nontrivial structure-determining motives can be built into helical porphyrin(1.1.1.1)-like skeletons which opens a route to a whole class of three-dimensional helical porphyrinoids, including recently reported metallocenoporphyrinoids.[14] Significantly, the metallocene unit contributes to metallomacrocyclic aromaticity in a similar fashion as various commonly incorporated "two-dimensional" hetero- and carbocyclic rings.

Here, in searching for general routes to helical aceneporphyrinoids, we report on the synthesis, structure, and spectroscopic properties of 22-hetero-1,5-naphthiporphyrins. An incorporation of a sterically demanding 1,5-linked naphthalene unit into a porphyrin(1.1.1.1) frame has been approached. The chosen linker fits to the geometry of macrocycles and evidently enforces the helical architecture.

The crucial step in the synthesis of 22-hetero-1,5-naphthiporphyrins is the construction of the condensation substrate, that is, 1,5-bis(phenylhydroxymethyl)naphthalene **2** (Scheme 2), which is a suitable synthon to introduce the 1,5-naphthylene ring into a porphyrin-like skeleton.

The method chosen consists of the Friedel–Crafts reaction between naphthalene and benzoyl chloride, followed by the reduction of the resulting 1,5-dibenzoylnaphthalene **1** with lithium aluminum hydride. 1,5-Bis(phenylhydroxymethyl)-naphthalene **2** was subsequently reacted with an excess of pyrrole to yield tripyrrane analogue 1,5-bis(phenyl(2-pyrolyl)-methyl)naphthalene **3**.

22-Thia-1,5-naphthiporphyrin has been obtained in a simple modification of the [3 + 1] synthesis[10,15] described for *p*-benziporphyrin,[3,12] 1,4-naphthiporphyrins,[7,10] and heterocarbaporphyrins[6,7] (Scheme 3). A condensation of **3** with 2,5-bis(tolylhydroxymethyl)thiophene **4**-S in dichloromethane, catalyzed by boron trifluoride diethyl etherate and followed by oxidation with DDQ, resulted in the formation of 22-thia-1,5-naphthiporphyrin **5**-S with 19% yield. Analogous reactions using 2,5-bis(tolylhydroxymethyl)selenophene **4**-Se, 2,5-bis-(phenylhydroxymethyl)tellurophene **4**-Te_a, and 2,5-bis(4-methoxyphenylhydroxymethyl)tellurophene **4**-Te_b afforded

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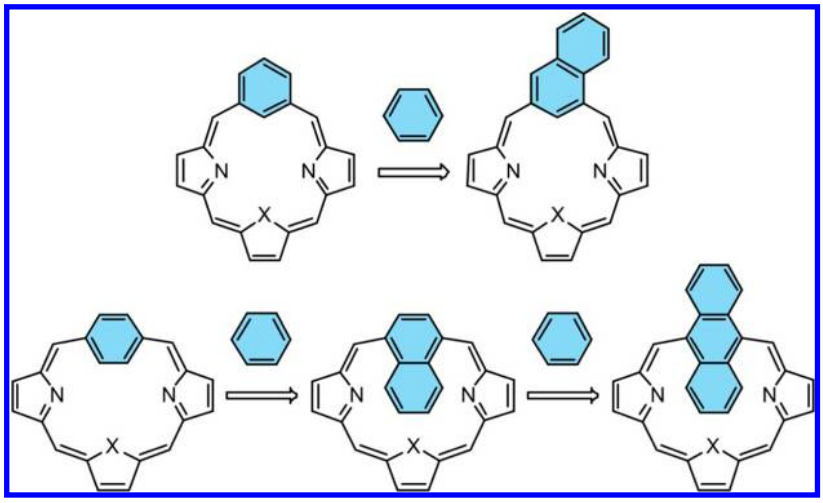
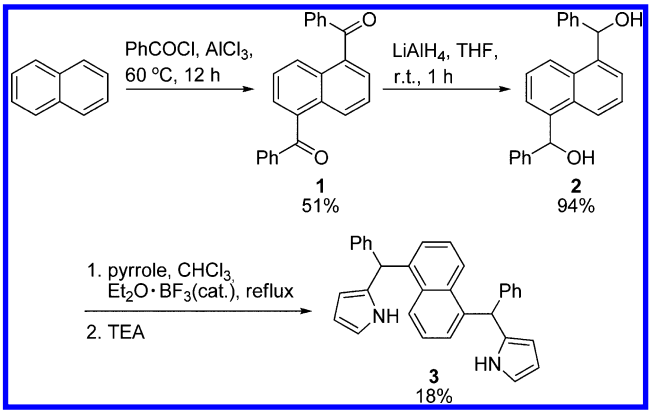
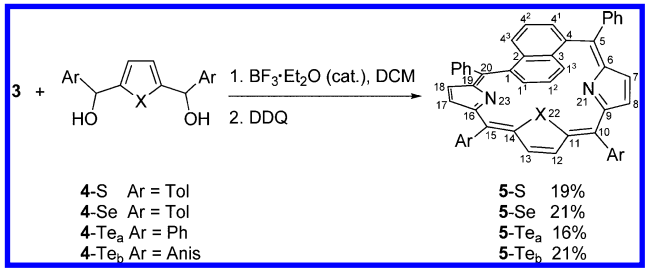
Scheme 1. Iterative Approach toward Aceneporphyrinoids



Scheme 2. Synthesis of 3



Scheme 3. Synthesis of 22-Hetero-1,5-naphthiporphyrins 5-X (Anis-4-methoxyphenyl)



22-selena-1,5-naphthiporphyrin **5**-Se (yield 21%) and 22-tellura-1,5-naphthiporphyrins **5**-Te_a (yield 16%) and **5**-Te_b (yield 21%), respectively.

X-ray analyses have been performed for compounds **5**-S and **5**-Se. The representative molecular structure of **5**-Se is visualized in Figure 1.

5-S and **5**-Se demonstrate the slight tilt of the naphthalene moiety toward the center of the molecule (Figure 1 and Figure S1 in Supporting Information). The dihedral angles between the naphthalene ring and the four *meso*-carbon atom mean plane (C_{4meso}) equal ca. 81.7° for **5**-S and 82.0° for **5**-Se. To accommodate the 1,5-naphthalene moiety, the dihedral angle between C(14)C(11)C(5) and C(11)C(14)C(20) planes of incorporated thiatriphyrin (**5**-S 17.7°) and selenatriphyrin (**5**-Se 16.2°) fragments has to increase considerably as compared

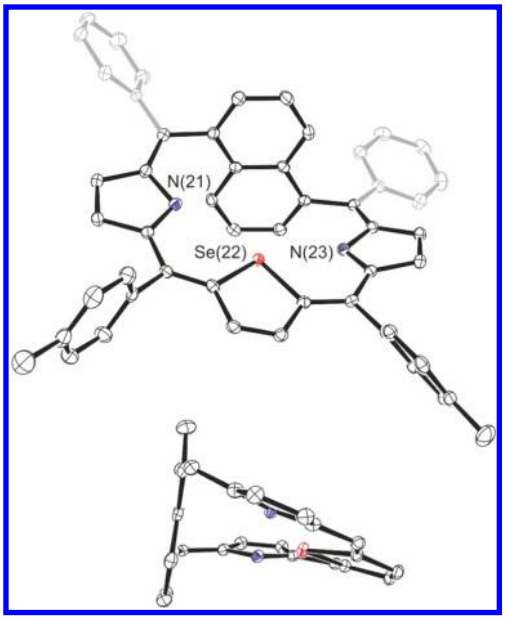


Figure 1. Molecular structure of **5**-Se (top, perspective view; bottom, side view). Perimeter hydrogen atoms and *meso*-aryls are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

to those of 1,4-thianaphthiporphyrin (1.6°)[7] and slightly folded 21-thiaporphyrin (5.8°),[16] exceeding even the values reported for helical ruthenocenothiaporphyrin (13.3°).[14] **5**-S and **5**-Se acquire a helical geometry which is similar to the geometry of porphyrinoids, which contain an analogous tripyrrane-like linker and a three-dimensional spacer.[14] π-Bonds within the thia(selena)tripyrrane subunit are largely localized in the manner indicated by the valence structure of these porphyrinoids (Scheme 3). At the same time, the bond lengths in the naphthalene moiety preserve the pattern of regular naphthalene. The C(20)−C(1) and C(4)−C(5) distances approach the single-bond limit for $C(sp^2)-C(sp^2)$.

There is an appreciable effect of the conjugation on the thiophene and selenophene fragments. The bond distances within the heterocyclopentadiene rings are altered. Thus the $C_\alpha-C_\beta$ bond lengths (**5**-S, 1.434(3), 1.432(3) Å; **5**-Se, 1.437(3), 1.442(3) Å) are longer than the $C_\beta-C_\beta$ distances (**5**-S, 1.339(3) Å; **5**-Se, 1.347(3) Å), whereas the reverse is true for thiophene[17] and selenophene.[18]

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The UV−vis electronic spectrum of **5**-S (Figure 2) demonstrates three bands at 352 (4.49), 401 (4.53), and 643 (4.32) nm. Spectra of **5**-Se and **5**-Te resemble the spectrum of **5**-S, although the distinctive red shift of the low energy band is detected for **5**-Te. In fact, the spectroscopic features of **5**-X resemble those for nonaromatic 6,11,16,21-tetraphenyl-*m*-benziporphyrin or 3-aza-24-thiabenziporphyrin.[2,19] The low extinction coefficients are consistent with the nonaromatic character of these macrocycles.

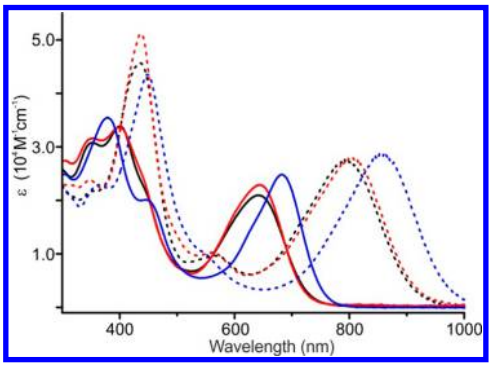

Figure 2. Electronic spectra (DCM, 298 K) of **5**-S (black solid line), **5**-Se (red solid line), **5**-Te_b (blue solid line), and their dications (dashed lines of the same color).

The titration of dichloromethane solutions of **5**-S, **5**-Se, and **5**-Te with TFA has been followed by UV−vis electronic spectroscopy (Figures S27−S30 in Supporting Information), revealing isosbestic points between the neutral and the dicationic form. The acid titration is accompanied by the distinct color change from green to orange. Patterns of UV−vis electronic spectra of (**5**-S)H_2^{2+}, (**5**-Se)H_2^{2+}, and (**5**-Te)H_2^{2+} resemble that of neutral forms, although remarkable red shifts have been detected for the low energy band (Figure 2).

Enantiomers of **5**-Te_b have been separated by HPLC using a chiral column where two fractions were observed with different retention times (Figure S31 in Supporting Information). CD experiments demonstrate the optical activity as complementary spectra of enantiomers (Figure 3). Once separated, both enantiomers remain stable and do not show any evidence of racemization.

Porphyrinoids **5**-S, **5**-Se, and **5**-Te cannot take on the macrocyclic aromaticity typical of porphyrins because of structural constraints. In particular, the nearly orthogonal

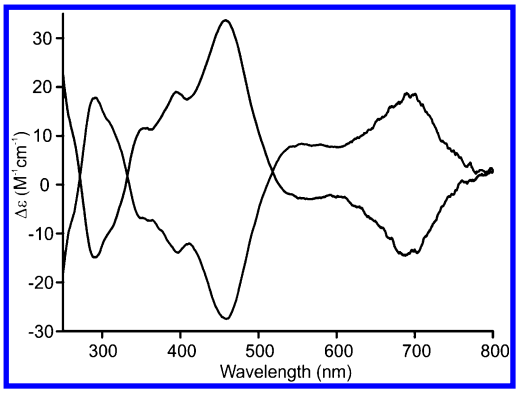

Figure 3. CD spectra recorded for enantiomers of **5**-Te_b (DCM, 298 K).

position of 1,5-naphthylene with respect to the C_{4meso} mean plane completely blocks macrocyclic π-delocalization while retaining unperturbed naphthalene aromaticity. Consequently, the ^{1}H NMR spectra of **5**-X show resonances at positions consistent with nonaromatic structures (Figure 4). The macrocyclic aromatic ring current effect is absent for **5**-S, **5**-Se, and **5**-Te, as clearly illustrated by the positions of pyrrole and heterocyclopentadiene resonances assigned by two-dimensional experiments. The marked differentiation of H(7,18) and H(8,17) chemical shifts (**5**-S, ca. 0.8 ppm; **5**-Se, 0.9 ppm; and **5**-Te_a, 0.8 ppm) is caused by the peculiar orientation of *meso*-substituents as shown in the molecular structures (Figure 1 and Figure S1 in Supporting Information). Because of the unique conformation of the macrocycle, phenyl rings at positions 5 and 20 acquire conformation characterized by the $C_{ortho}C_{ipso}C_{meso}C_{\alpha}$ torsional angle equal to ca. 45°, whereas the tolyl rings at positions 10 and 15 are nearly orthogonal. Eventually this results in deshielding of the 7,18-hydrogen atoms with respect to the 8,17-hydrogen atoms. The analogous differentiation of chemical shifts was also reported for tetraaryl-*m*-benziporphyrin and tetraaryl-3-aza-*m*-benziporphyrin.[2,19] Consistent with helical structures of **5**-X, the frozen rotation of *meso*-aryls resulted in differentiation of ortho resonances (see Figures S8−S10 in Supporting Information). The ^{1}H chemical shift values of heterocyclopentadiene and pyrrole β-hydrogens are in the range determined for other nonaromatic fully conjugated systems.[2,19] The thiophene, selenophene, and tellurophene moieties embedded in macrocyclic structures show chemical shifts similar to those seen for **4**-S, **4**-Se, and **4**-Te, respectively.

Results of ^{1}H NMR spectroscopic titrations carried out by addition of TFA to solutions of 22-hetero-1,5-naphthiporphyrins **5**-X in $CDCl_3$ are shown in Figure 4 (trace D) and Figure S7 in Supporting Information. Under these conditions (chloroform-*d*, 220 or 300 K), proton exchange processes involving **5**-X and (**5**-X)H_2^{2+} (X = S, Se, Te) are fast on the ^{1}H NMR time scale, and consequently only a smooth change of the chemical shifts can be observed in the whole titration range. Addition of more than 2 equiv of TFA does not cause further changes of chemical shifts affording progressive broadening of the signals.

In conclusion, in the course of these studies we have demonstrated that 1,5-naphthylene can be built into a helical heteroporphyrin(1.1.1.1)-like skeleton, opening a route to three-dimensional porphyrinoids. The steric constraints reflecting the specific substitution mode of the acene building block imposed the specific helical conformation of the bridging heterotripyrrin linker, similar to what has been described for metallocenoporphyrinoids[14] or morpholinochlorins.[20] The nearly orthogonal conformation of 1,5-naphthylene with respect to the C_{4meso} mean plane blocks efficiently the macrocyclic π-delocalization, rendering 22-hetero-1,5-naphthiporphyrins nonaromatic, which remain in contrast to isomeric 24-thia-1,4-naphthiporphyrin; β-H and NH chemical shifts resemble these of carbaporphyrinoids in the borderline cases of porphyrinoid aromaticity.[7]

The chemistry presented herein provides many opportunities for further study, such as the synthesis of systems with expanded macrocyclic cores, more extensive π-conjugation, and metalation which facilitates the specific close spatial metal ion−1,5-naphthylene proximity.

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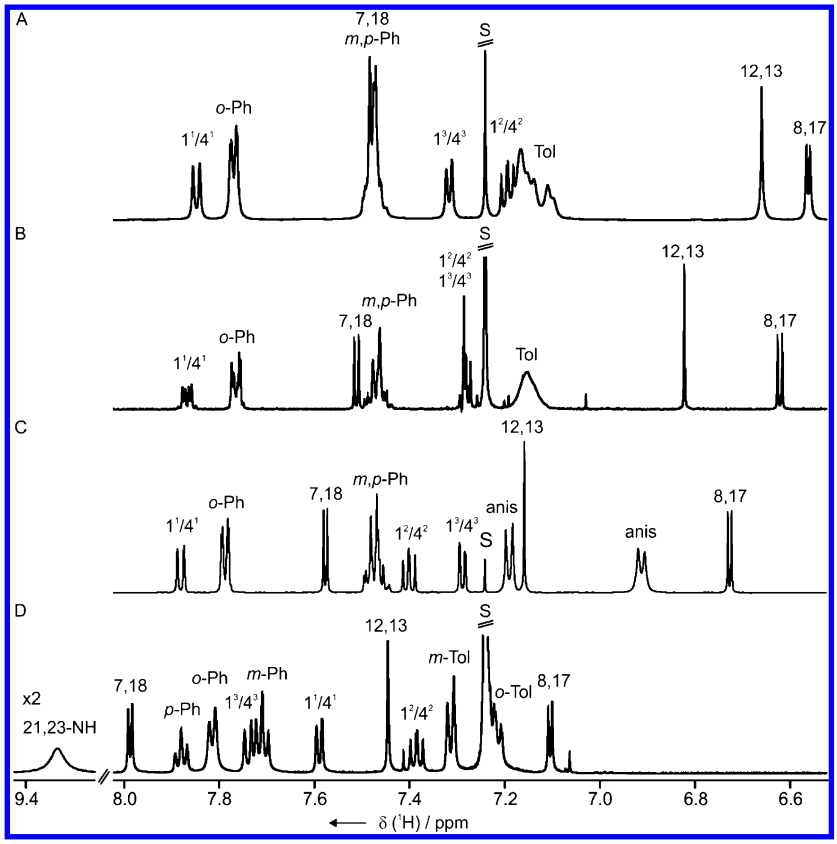

Figure 4. ^{1}H NMR spectra (chloroform-*d*, 298 K (traces A, B, and C), 220 K (trace D)) of **5**-S (A), **5**-Se (B), **5**-Te$_b$ (C), and (**5**-Se)H$_2^{2+}$ (D). Resonance assignments (obtained from COSY and NOESY experiments) follow the numbering scheme given in Scheme 3. Methyl and methoxyl peaks are not shown.

EXPERIMENTAL SECTION

Dichloromethane and pyrrole were distilled over calcium hydride. Chloroform-*d* was dried directly before use by being run through a basic alumina column. Reagents not listed here were used as received.

2,5-Bis(tolylhydroxymethyl)thiophene **4**-S, 2,5-bis(phenylhydroxymethyl)tellurophene **4**-Te$_a$, and 2,5-bis(4-methoxyphenylhydroxymethyl)tellurophene **4**-Te$_b$ were synthesized according to previously described procedures.[21,22]

2,5-Bis(tolylhydroxymethyl)selenophene 4-Se. Synthesized as described in the literature, but *p*-tolylaldehyde (2.3 mL, 19 mmol) was used instead of benzaldehyde.[23] The crude product was chromatographed on silica gel (70−230 mesh) using dichloromethane as eluant to remove nonpolar impurities and then 5% methanol−dichloromethane to elute **4**-Se. The solvent was removed under reduced pressure yielding **4**-Se. Recrystallization of **4**-Se from dichloromethane−hexane afforded **4**-Se as a white, crystalline solid. mp: 128 °C. Yield: 702 mg (25%). ^{1}H NMR (500 MHz, chloroform-*d*, 300 K, pair of diastereomers): δ 7.29 and 7.28 (m, 4H, Tol), 7.13 (m, 4H, Tol), 6.83 (s, 2H, selenophene), 5.87 (m, 2H, **CH**OH), 2.45 (m, 2H, CH**OH**), 2.32 (s, 6H, **CH$_3$**). ^{13}C NMR (126 MHz, chloroform-*d*, 300 K, pair of diastereomers): δ 155.9 and 155.8, 140.5 and 140.4, 137.72 and 137.70, 129.2, 126.2, 126.1, 126.0, 74.18 and 74.16, 21.1. HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{20}NaO_2Se^+$ 395.0521; found 395.0520.

1,5-Dibenzoylnaphthalene (1). Synthesized as described, but with some significant modifications.[24] Aluminum chloride (26.7 g, 0.2 mol) was suspended in benzoyl chloride (14.5 mL, 0.12 mol) placed in a 500 mL round-bottomed flask equipped with a magnetic stirring bar and immersed in an oil bath. The setup was fitted with a reflux condenser, and the solution was heated to 70 °C and then cooled to 60 °C. Four portions of naphthalene (6.4 g, 0.05 mol; one portion: 1.6 g) were added every 1 h. The reaction mixture was protected from moisture (a tube with calcium chloride on the top of a condenser) and then was stirred overnight. The reaction mixture was cooled to room temperature, and the process was quenched by cautious addition of a hydrochloric acid/brine solution (100 mL, 2/3 v/v). Subsequently, the reaction mixture was stirred with 200 mL of dichloromethane for 1 h. The organic phase was separated, washed with water, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was washed with acetone on a sintered glass funnel, yielding a yellowish-white, amorphous solid. Yield: 8.5 g (51%). ^{1}H NMR (500 MHz, chloroform-*d*, 300 K): δ 8.23 (ABC spin system, 2H, naphthalene), 7.87 (d, 4H, ^3J = 7.8 Hz, *o*-Ph), 7.62−7.59 (m, 4H, naphthalene, *p*-Ph), 7.52 (ABC spin system, 2H, naphthalene), 7.46 (t, 4H, ^3J = 7.8 Hz, *m*-Ph). ^{13}C NMR (126 MHz, chloroform-*d*, 300 K): δ 197.7, 138.0, 136.9, 133.5, 131.2, 130.4, 128.6, 128.5, 127.9, 126.6. HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{17}O_2^+$ 337.1223; found 337.1218.

1,5-Bis(phenylhydroxymethyl)naphthalene (2). In a 1000 mL round-bottomed flask equipped with a magnetic stirring bar and immersed in an oil bath, 1,5-dibenzoylnaphthalene **1** (6.0 g, 0.018 mol) was dissolved in THF (500 mL) under nitrogen. Solid lithium aluminum hydride (1.7 g, 2.5 equiv) was then added in small portions to avoid excessive gas evolution. The reaction mixture was then stirred for 1 h and then the reaction quenched by cautious addition of water (3 mL) followed by 2 M aqueous NaOH (5 mL). The reaction mixture was filtered. The solvent was removed on a rotary evaporator to afford a yellowish, amorphous solid. Yield: 5.7 g (94%). ^{1}H NMR (500 MHz, chloroform-*d*, 300 K, pair of diastereomers): δ 8.04 and 8.03 (two ABC spin systems, 2H, naphthalene), 7.60 (two ABC spin systems, 2H, naphthalene), 7.45−7.41 (ABC spin system, 2H, naphthalene), 7.39−7.38 (m, 4H, *o*-Ph), 7.33−7.30 (m, 4H, *m*-Ph), 7.26−7.24 (m, 2H, *p*-Ph, signal is partially covered with the solvent peak), 6.55−6.53 (m, 2H, **CH**OH), 2.29 and 2.27 (2d, 2H, ^3J = 4.0 Hz, CH**OH**). ^{13}C NMR (126 MHz, chloroform-*d*, 300 K, pair of diastereomers): δ 143.1, 139.4, 131.24 and 131.21, 128.58 and 128.56, 127.75 and 127.71, 127.1 and 127.0, 125.61 and 125.59, 124.53 and

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124.46, 124.4 and 124.3, 73.9 and 73.8. HRMS (ESI-TOF): m/z [M − OH]$^+$ calcd for $C_{24}H_{19}O^+$ 323.1430; found 323.1421.

1,5-Bis(phenyl(2-pyrolyl)methyl)naphthalene (3). In a 250 mL round-bottomed flask equipped with a reflux condenser and magnetic stirring bar, 1,5-bis(phenylhydroxymethyl)naphthalene **2** (1.21 g, 3.5 mmol) was dissolved in a mixture of dry pyrrole (10 mL, 145 mmol) and chloroform (15 mL). The solution was purged with nitrogen for 20 min. Subsequently, boron trifluoride diethyl etherate (250 μL) was added, the setup was fitted with a reflux condenser, and the solution was refluxed for 48 h in a nitrogen atmosphere. The solution was neutralized by addition of triethylamine (1−2 mL). Solvents were removed using a rotary evaporator, and the crude residue was chromatographed on silica gel (70−230 mesh) using the solution of 1% triethylamine in dichloromethane as eluant. The desired product eluted as the first fraction. The solvent was removed under reduced pressure, yielding **3** as a white, amorphous solid. Yield: 273 mg (18%). ^{1}H NMR (500 MHz, chloroform-*d*, 300 K, pair of diastereomers): δ 7.98 and 7.97 (two ABC spin systems, 2H, naphthalene), 7.76 (b, 2H, NH), 7.32 (ABC spin system, 2H, naphthalene), 7.28−7.26 (m, 4H, *m*-Ph), 7.23−7.20 (m, 2H, *p*-Ph), 7.18−7.16 (m, 4H, *o*-Ph), 7.01 (ABC spin system, 2H, naphthalene), 6.67 (m, 2H, pyrrole), 6.22 (2s, 2H, CH), 6.14 (m, 2H, pyrrole), 5.80 (m, 2H, pyrrole). ^{13}C NMR (126 MHz, chloroform-*d*, 300 K, pair of diastereomers): δ 142.9, 139.73 and 139.72, 133.4, 132.19 and 132.16, 129.02 and 128.99, 128.6, 126.7, 126.6, 125.7, 123.3, 117.14 and 117.12, 108.42 and 108.40, 108.31 and 108.27, 46.99 and 46.97. HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{32}H_{26}N_2Na^+$ 461.1988; found 461.1983.

Synthesis of 5-X: A General Protocol for Condensation. **3** (876 mg, 2 mmol in the case of **5**-S; 438 mg, 1 mmol in the case of **5**-Se, **5**-Te$_a$, and **5**-Te$_b$) and **4**-S (648 mg, 2 mmol), **4**-Se (371 mg, 1 mmol), **4**-Te$_a$ (394 mg, 1 mmol), or **4**-Te$_b$ (454 mg, 1 mmol) were added to dry dichloromethane (900 mL) under nitrogen. Boron trifluoride diethyl etherate (150 μL in the case of **5**-S, 100 μL in other cases) was then added, and the reaction mixture was protected from light and stirred for 2 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 1362 mg, 6 mmol in the case of **5**-S and 681 mg, 3 mmol in other cases) was subsequently added, and the reaction mixture was stirred for an additional 0.5 h. The solvent was evaporated under reduced pressure, and the dark residue was subjected to chromatography (grade II alumina, dichloromethane). The desired product was eluted as a green band. Next steps of separation are described specifically for **5**-S, **5**-Se, **5**-Te$_a$, and **5**-Te$_b$.

5,20-Diphenyl-10,15-ditolyl-22-thia-1,5-naphthiporphyrin (5-S). 21,23-Dithiaporphyrin formed also in the course of condensation has been separated from **5**-S using column chromatography (silica gel 70−230 mesh) with dichloromethane as eluant. The second band eluted with 5% methanol−dichloromethane that contained **5**-S. Two following column chromatographies (grade II alumina) using dichloromethane−hexane as eluant (v/v 3/2 then 7/3) and the subsequent recrystallization from dichloromethane-methanol afforded **5**-S as a dark green, crystalline solid. Yield: 277 mg (19%). ^{1}H NMR (500 MHz, chloroform-*d*, 300 K): δ 7.85 (ABC spin system, 2H, $1^1/4^1$-H), 7.78−7.76 (m, 4H, 5,20-*o*-Ph), 7.50−7.44 (m, 6H, 5,20-*m*,*p*-Ph), 7.48 (d, 2H, ^3J = 4.8 Hz, 7,18-H), 7.31 (ABC spin system, 2H, $1^3/4^3$-H), 7.19 (ABC spin system, 2H, $1^2/4^2$-H), 7.16−7.09 (m, 8H, 10,15-Tol), 6.66 (s, 2H, 12,13-H), 6.56 (d, 2H, ^3J = 4.8 Hz, 8,17-H), 2.37 (s, 6H, 10,15-Tol-CH$_3$). ^{13}C NMR (151 MHz, chloroform-*d*, 298 K): δ 168.7, 158.1, 153.3, 150.1, 140.2, 139.5, 137.2, 137.0, 136.4, 133.4, 131.9, 131.6, 131.1, 131.0, 130.6, 129.4, 129.3, 128.6, 128.5, 127.3, 124.3, 122.5, 21.2. HRMS (ESI-cyclotron): m/z [M + H]$^+$ calcd for $C_{52}H_{37}N_2S^+$ 721.2672; found 721.2664. UV−vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 352 (4.49), 401 (4.53), 643 (4.32).

5,20-Diphenyl-10,15-ditolyl-22-thia-1,5-naphthiporphyrin Dication (5-S). H_2^{2+} UV−vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 354 (4.34), 434 (4.66), 569 (3.98), 797 (4.44).

5,20-Diphenyl-10,15-ditolyl-22-selena-1,5-naphthiporphyrin (5-Se). **5**-Se has been isolated by column chromatography (grade II alumina) with dichloromethane−hexane as eluant (v/v 7/3 then 3/2). Subsequently, the recrystallization from dichloromethane−methanol afforded **5**-Se as a dark green, crystalline solid. Yield: 164 mg (21%). ^{1}H NMR (500 MHz, chloroform-*d*, 300 K): δ 7.87 (ABC spin system, 2H, $1^1/4^1$-H), 7.77−7.55 (m, 4H, 5,20-*o*-Ph), 7.51 (d, 2H, ^3J = 4.8 Hz, 7,18-H), 7.49−7.44 (m, 6H, 5,20-*m*,*p*-Ph), 7.29−7.26 (m, two ABC spin systems, 4H, $1^2/4^2$,$1^3/4^3$-H), 7.15 (m, 8H, 10,15-Tol), 6.82 (s, 2H, 12,13-H), 6.62 (d, 2H, ^3J = 4.8 Hz, 8,17-H), 2.37 (s, 6H, 10,15-Tol-CH$_3$). ^{13}C NMR (151 MHz, chloroform-*d*, 280 K): δ 169.7, 157.5, 154.9, 150.0, 140.1, 139.3, 138.2, 137.2, 136.6, 133.9, 132.6, 131.8, 131.4, 131.1, 131.0, 130.4, 129.6, 128.3, 128.7, 127.2, 125.2, 123.4, 21.4. HRMS (ESI-cyclotron): m/z [M + H]$^+$ calcd for $C_{52}H_{37}N_2Se^+$ 769.2116; found 769.2129. UV−vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 355 (4.50), 397 (4.53), 643 (4.36).

5,20-Diphenyl-10,15-ditolyl-22-selena-1,5-naphthiporphyrin Dication ((5-Se)H$_2^{2+}$). ^{1}H NMR (600 MHz, chloroform-*d*, 220 K): δ 9.33 (b, 2H, 21,23-NH), 7.99 (d, 2H, ^3J = 5.0 Hz, 7,18-H), 7.88 (t, 2H, ^3J = 7.5 Hz, 5,20-*p*-Ph), 7.81 (d, 4H, ^3J = 7.5 Hz, 5,20-*o*-Ph), 7.74 (ABC spin system, 2H, $1^3/4^3$-H), 7.71 (t, 4H, ^3J = 7.5 Hz, 5,20-*m*-Ph), 7.59 (ABC spin system, 2H, $1^1/4^1$-H), 7.44 (s, 2H, 12,13-H), 7.38 (ABC spin system, 2H, $1^2/4^2$-H), 7.31 (d, 4H, ^3J = 8.1 Hz, 10,15-*m*-Tol), 7.23−7.20 (m partially covered with solvent signal, 4H, 10,15-*o*-Tol), 7.10 (d, 2H, ^3J = 5.0 Hz, 8,17-H), 2.43 (s, 6H, 10,15-Tol-CH$_3$). UV−vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 302 (4.36), 348 (4.38), 437 (4.71), 559 (4.01), 809 (4.44).

5,10,15,20-Tetraphenyl-22-tellura-1,5-naphthiporphyrin (5-Te$_a$). **5**-Te$_a$ has been isolated using column chromatography (grade II alumina) with dichloromethane−hexane as eluant (v/v 4/1). Subsequently, the recrystallization from dichloromethane−methanol afforded **5**-Te$_a$ as a dark green, crystalline solid. Yield: 125 mg (16%). ^{1}H NMR (600 MHz, chloroform-*d*, 298 K): δ 7.88 (ABC spin system, 2H, $1^1/4^1$-H), 7.79−7.77 (m, 4H, 5,20-*o*-Ph), 7.51 (d, 2H, ^3J = 4.8 Hz, 7,18-H), 7.49−7.44 (m, 6H, 5,20-*m*,*p*-Ph), 7.41 (ABC spin system, 2H, $1^2/4^2$-H), 7.38−7.35 (m, 4H, 10,15-Ph), 7.33−7.30 (m, 2H, 10,15-Ph), 7.29 (ABC spin system, 2H, $1^3/4^3$-H), 7.26 (d, ^3J = 7.4 Hz, 4H, 10,15-Ph), 7.11 (s, 2H, 12,13-H), 6.69 (d, 2H, ^3J = 4.8 Hz, 8,17-H). ^{13}C NMR (151 MHz, chloroform-*d*, 298 K): δ 170.7, 156.2, 152.9, 149.1, 142.5, 139.9, 139.3, 139.0, 137.6, 134.5, 131.5, 131.4, 130.9 (b), 130.7, 130.2 (b), 129.5, 128.7, 127.9, 127.2, 126.9, 126.7, 124.4. HRMS (ESI-cyclotron): m/z [M + H]$^+$, calcd for $C_{50}H_{33}N_2Te^+$ 791.1700; found 791.1720. UV−vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 373 (4.45) sh, 420, 672 (4.31).

5,10,15,20-Tetraphenyl-22-tellura-1,5-naphthiporphyrin Dication ((5-Te$_a$)H$_2^{2+}$). ^{1}H NMR (600 MHz, chloroform-*d*, 298 K): δ 7.88 (d, 2H, ^3J = 5.0 Hz, 7,18-H), 7.79−7.78 (m, 6H, 5,20-*o*-Ph and $1^1/4^1$-H or $1^3/4^3$-H), 7.69 (t, 2H, ^3J = 7.7 Hz, 5,20-*p*-Ph), 7.61 (t, 4H, ^3J = 7.7 Hz, 5,20-*m*-Ph), 7.56 (ABC spin system, 2H, $1^1/4^1$-H or $1^3/4^3$-H), 7.49−7.47 (m, 8H, 10,15-Ph, $1^2/4^2$-H), 7.46 (s, 2H, 12,13-H), 7.27−7.26 (m, 4H, 10,15-Ph), 6.95 (d, 2H, ^3J = 5.0 Hz, 8,17-H).

5,20-Diphenyl-10,15-dianisyl-22-tellura-1,5-naphthiporphyrin (5-Te$_b$). **5**-Te$_b$ has been isolated in two following chromatographies on alumina (active alumina) with dichloromethane and then grade II alumina with dichloromethane−hexane as eluant (v/v 4/1). Subsequently, the recrystallization from dichloromethane−methanol afforded **5**-Te$_b$ as a dark green, crystalline solid. Yield: 181 mg (21%).

Separation of enantiomers **5**-Te$_b$ and **5**-Te$_b$′ was accomplished using the HPLC system equipped with an analytical column (25 cm length, 4.6 mm i.d.) packed with 5 μm silica gel coated with covalently bound (*S*)-valine and dinitroaniline. The eluant system was dichloromethane−hexane (v/v 1/5). ^{1}H NMR (600 MHz, chloroform-*d*, 298 K): δ 7.88 (ABC spin system, 2H, $1^1/4^1$-H), 7.79−7.78 (m, 4H, 5,20-*o*-Ph), 7.57 (d, 2H, ^3J = 4.8 Hz, 7,18-H), 7.49−7.44 (m, 6H, 5,20-*m*,*p*-Ph), 7.40 (ABC spin system, 2H, $1^2/4^2$-H), 7.29 (ABC spin system, 2H, $1^3/4^3$-H), 7.19 (d, 4H, ^3J = 8.6 Hz, 10,15-*o*/*m*-anisyl), 7.16 (s, 2H, 12,13-H), 6.91 (m, 4H, 10,15-*o*/*m*-anisyl), 6.72 (d, 2H, ^3J = 4.8 Hz, 8,17-H), 3.83 (s, 6H, 10,15-CH$_3$-anisyl). ^{13}C NMR (151 MHz, chloroform-*d*, 298 K): δ 171.0, 158.8, 156.2, 152.9, 148.9, 142.4, 140.4, 139.0, 137.2, 134.4, 132.2 (b), 132.8, 131.5, 131.4, 130.8, 129.5, 128.7, 126.9, 126.7, 124.4, 113.3, 55.3. HRMS (ESI-cyclotron): m/z [M + H]$^+$ calcd for $C_{52}H_{37}N_2TeO_2^+$ 851.1912; found 851.1929. UV−vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 378 (4.55), 444 (4.30), 681 (4.39).

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5,20-Diphenyl-10,15-dianisyl-22-tellura-1,5-naphthiporphyrin Dication ($(5\text{-}Te_b)H_2^{2+}$). UV−vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 363 (4.36), 448 (4.64), 853 (4.46).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of crystal data, bond lengths, angles, anisotropic thermal parameters (cif file), a full set of NMR and UV−vis electronic spectra, and HRMS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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