# Synthesis of 21,23-Selenium- and Tellurium-Substituted 5-Porphomethenes, 5,10-Porphodimethenes, 5,15-Porphodimethenes, and Porphotrimethenes and Their Interactions with Mercury

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# Synthesis of 21,23-Selenium- and Tellurium-Substituted 5-Porphomethenes, 5,10-Porphodimethenes, 5,15-Porphodimethenes, and Porphotrimethenes and Their Interactions with Mercury

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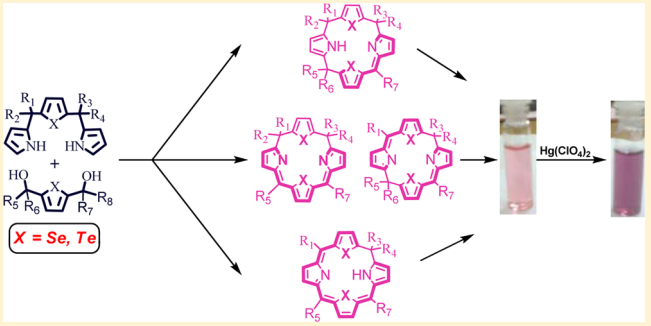
Supporting Information

**ABSTRACT:** The 3+1 condensation of symmetrical 16-Selena/telluratripyrranes with symmetrical selenophene-2,5-diols/tellurophene-2,5-diols in the presence of $BF_3$-etheratre or $BF_3$-methanol followed by oxidation with DDQ gave 5,10-porphodimethenes, whereas the process with unsymmetrical selenophene-2,5-diols/tellurophene-2,5-diols gave 5-porphomethenes. In addition, the reaction of unsymmetrical 16-Selena/telluratripyrranes with symmetrical selenophene-2,5-diols/tellurophene-2,5-diols gave the corresponding porphotrimethenes, whereas the process with unsymmetrical selenophene-2,5-diols/tellurophene-2,5-diols gave the 5,15-porphodimethenes. The structures of different products were characterized by IR, $^1$H and $^{13}$C NMR, $^1$H−$^1$H COSY, CHN analysis, and mass spectrometry. The binding of mercury with the calix[4]phyrins mentioned above had been observed in the decreasing order of porphodimethenes > porphomethenes > porphotrimethenes by UV−vis and $^1$H NMR spectroscopy.




## INTRODUCTION

Porphomethenes, porphodimethenes, and porphotrimethenes are the classes of calixphyrins in which porphomethene [calix(4)phyrin-(**1**.1.1.1)] contains one sp$^2$-hybridized *meso*-carbon atom and three sp$^3$-hybridized *meso*-carbon atoms, porphodimethene [calix(4)phyrin-(**1**.1.1.1 and **1**.1.1.1)] contains two sp$^2$-hybridized and two sp$^3$-hybridized *meso*-carbon atoms, and porphotrimethene [calix(4)phyrin-(**1**.1.1.1)] contains three sp$^2$-hybridized *meso*-carbon atoms and one sp$^3$-hybridized *meso*-carbon atom (Figure 1).[1] The presence of sp$^3$-hybridized *meso*-carbon centers disrupts the $\pi$-conjugation and allows the macrocycle to adapt a nonplanar conformation;[2] because of the presence of the sp$^3$-hybridized unit, these compounds display an intriguing multielectron redox chemistry.[3] Calix[4]phyrins consist of the intermediate structure of porphyrin and calix[4]pyrrole; thus, they have properties analogous to those of both porphyrins and calix[4]pyrroles and play diverse roles as metal ion receptors[4] and anion-complexing agents[5] and reveal a rich coordination chemistry.[6] However, the lack of $\pi$-conjugation compromises the spectroscopic properties of these macrocycles in comparison to those of the porphyrins.[7] Naturally, calix[4]phyrins have been proposed as intermediates in the synthesis of chlorophyll *a*,[1b,c] heme P460,[8] chlorins,[9] and porphyrins.[9b] Calix[4]phyrin was recently identified as a potential chemical inhibitor of uroporphyrinogen decarboxylase and reduced the viability of cancer cells.[10] Calix[4]phyrins have been synthesized by reductive alkylation of porphyrins,[11] dealkylation of calix[4]-pyrroles,[12] oxidation of porphyrinogens,[13] and reduction of porphyrins.[14] The methods described above require expansive reagents, multistep synthesis, and vigorous reaction conditions.

Recently, calix[4]phyrins have been synthesized by reaction of 5,5-disubstituted dipyrromethane and aldehyde or by reaction of 5-substituted dipyrromethane and ketone under acidic conditions followed by oxidation with DDQ, chloranil, or $FeCl_3$ under mild conditions.[15] The introduction of different substituents at the sp$^2$- or sp$^3$-hybridized *meso* position[15] impacts calixphyrin's stability, structure, and spectroscopic, electrostatic, and anion and cation binding properties. Modification of the calix[4]phyrin core by replacement of one or two nitrogen atoms with donor atoms[15] (O, S, and P) leads to the synthesis of core-modified calix[4]phyrins.[16] The porphodimethenes are stable, and their properties have been extensively studied; on the other hand, core-modified porphomethenes and porphotrimethenes (Figure 1) have remained unexplored because of the instability and complexity of the synthesis.[17] Therefore, a similar development is anticipated for the calixphyrins with heavier chalcogen donor atoms such as selenium and tellurium, because of their "softness" and better $\sigma$-donor capacity compared to that of the lighter group 16 congeners. Selenium and tellurium

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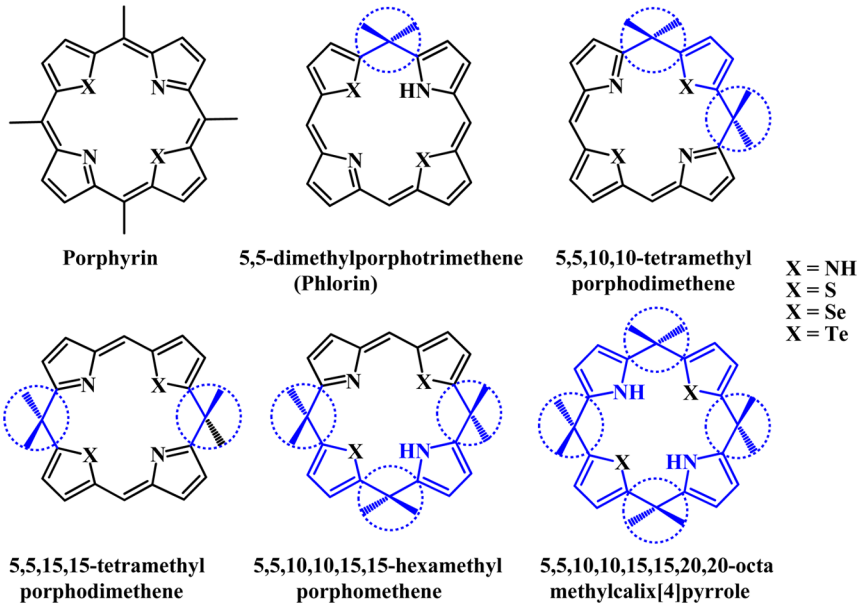
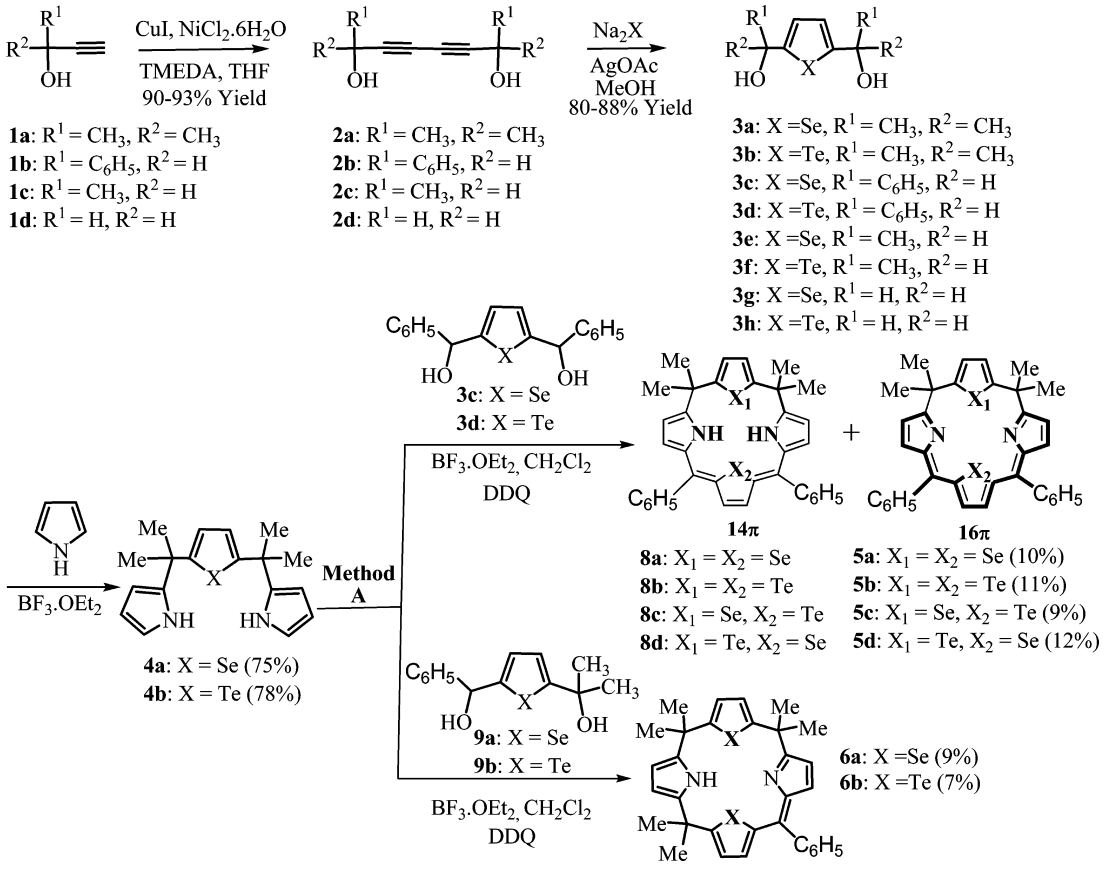



**Figure 1.** Structures of porphyrinoids.

**Scheme 1. Synthesis of Selenophene and Tellurophene Diols (3a–h), Tripyrranes (4a and 4b), 5,10-Porphodimethenes (5a–d), and Porphomethenes (6a and 6b)**




porphyrinoids and their derivatives keep attracting the attention of several research groups[18] beginning from the seminal contributions of Ulman and Manassen.[19] The absence of a suitable synthetic procedure, starting precursors, and instability toward air and light limit the chemistry of Se/Te calixphyrins. Recently, we had reported the first synthesis of Se/Te core-modified porphyrinogens and their coordination ability for the selective detection of $Hg^{2+}$ by UV–vis, fluorescence, and $^1H$ NMR spectroscopy.[20]

In this paper, we report the synthesis of novel 21,23-Se/Te-substituted porphomethenes, porphodimethenes, and porphotrimethenes via acid-catalyzed 3+1 condensation of 16-selenophene/tellurophene tripyrranes with corresponding selenophene-2,5-diols/tellurophene-2,5-diols. The interactions



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of *meso*-substituted calixphyrins with $Hg^{2+}$ ion have been examined by UV−vis, fluorescence, and $^1H$ NMR spectroscopy.

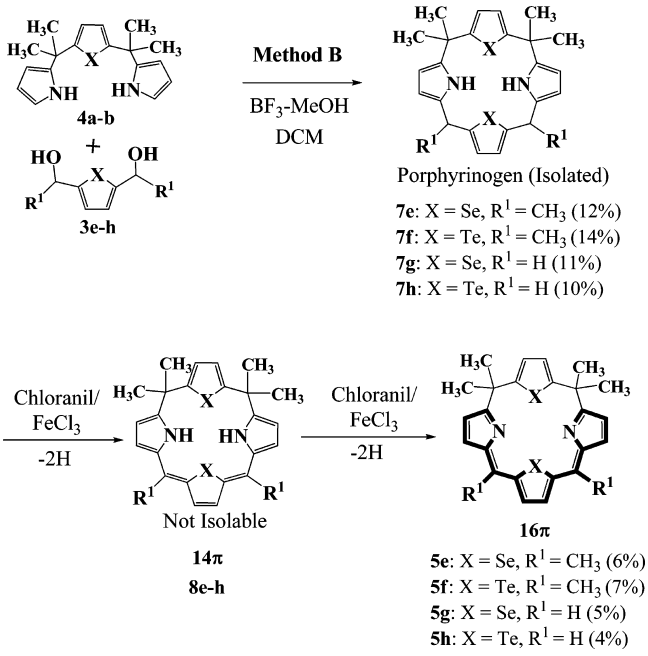
## RESULTS AND DISCUSSION

Acetylenic coupling is an important tool for the synthesis of natural products, pharmaceuticals, polymers, and nanomaterials.[21a] The two-step homocoupling of terminal alkynes using a stoichiometric amount of CuCl and $NH_4OH$ in an oxygen atmosphere was reported by Glaser in 1869.[21b,c] The one-step homocoupling using CuCl and TMEDA was reported in 1962.[21d] The CuI, $NiCl_2{\cdot}6H_2O$ system had been used for the homocoupling of 2-methylbut-3-yn-2-ol (**1a**) to give diynediol (**2a**).[22] Diynediol (**2a**) reacts with $Na_2Se$ in the presence of silver acetate to give 2,5-bis[hydroxy(dimethyl)methyl]-selenophene (**3a**). The structure of **3a** was fully confirmed by $^1H$ NMR and comparison of other spectroscopic data from the literature.[20] Similarly, other selenophene and tellurophene diols (**3b−h**) were synthesized and characterized. Selenophene diol **3a** reacts with an excess of pyrrole to give 16-selenatripyrrane (**4a**) in 75% yield. Similarly, 16-telluratripyrrane (**4b**) was synthesized and characterized by various spectroscopic techniques in 78% yield (Scheme 1).

The 3+1 condensation is an important method for the synthesis of selected porphyrins[15c] and core-modified porphyrins.[15,20,23] The 3+1 condensation of 1 equiv of tripyrranes (**4a**) with 1 equiv of corresponding diols (**3c**) in the presence of $BF_3$-etherate in dichloromethane (3.2 mM) at room temperature in 30 min, followed by treatment with 2.2 equiv of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), gave the new selenium core-modified 5,5,10,10-tetramethyl-15,20-bisphenyl-21,23-diselenaporphodimethene [**5a** (Scheme 1, method A)]. From the reaction, a mixture of two calixphyrins, **5a** and **8a**, was obtained. On the basis of the oxidation state of the $\pi$-conjugated moiety, **8a** is classified as a $2e^-$-oxidized product ($14\pi$) and **5a** as a $4e^-$-oxidized product ($16\pi$).[15b] In the high-resolution mass spectra, peaks corresponding to **8a** along with **5a** were observed (see the Supporting Information), and TLC analysis of the crude reaction mixture indicated that product **5a** was a predominant product of this condensation. However, all attempts to isolate **8a** from the reaction mixture resulted in its decomposition, and only $16\pi$-conjugated system **5a** was isolated by column chromatography in 10% yield. Even with a decrease in the amount of oxidant from 2 to 0.5 equiv, no significant improvements were observed in the yield of **8a**. The greater selectivity of the $16\pi$-conjugated system ($4e^-$-oxidized) and the instability of the $14\pi$-conjugated system ($2e^-$-oxidized) may be explained on the basis of weak hydrogen bonding interaction of the lone pair (Se) with the pyrrolic NH proton (X···H−N, where X = Se or Te) or its absence in **8a**; therefore, stabilization of the $14\pi$ system is not possible. Sulfur and oxygen core-modified calixphyrins showed greater stability of the $14\pi$-conjugated system in comparison to that of $16\pi$, which may arise from the repulsive or attractive electrostatic interactions between the core heteroatoms and the pyrrole NH groups.[15b,c] Similarly, the other porphodimethenes (**5b−d**) were synthesized and characterized by various spectroscopic techniques.

On the other hand, $sp^2$-hybridized *meso*-methyl-substituted porphodimethene (**5e** and **5f**) and $sp^2$-hybridized *meso*-unsubstituted porphodimethene (**5g** and **5h**) could not be synthesized by method A described above, and it led to the formation of a complex mixture. No corresponding porphodimethenes were detected by HRMS or in the UV−vis spectrum. In some cases, the HRMS analysis of the reaction mixture revealed the formation of desired porphyrinogen intermediates (**7e−h**), which disappeared without providing corresponding porphodimethene products upon oxidation with DDQ or *p*-chloranil. To understand the detailed mechanism of reaction, the intermediate porphyrinogens (**7e−h**) were isolated and characterized. These porphyrinogens (**7e−h**) were further oxidized under neutral conditions. Porphodimethenes (**5e−h**) were obtained by condensation of 1 equiv of tripyrranes (**4a** and **4b**) with 1 equiv of the corresponding diol (**3e−h**) in the presence of $BF_3$-methanol using dichloromethane as a solvent (3.2 mM) at 0 °C for 1 h, and then the reaction mixture was stirred at room temperature for 45 min (method B). The crude porphyrinogens were purified by silica gel column chromatography to afford white solids in 10−14% yield. The methyl-substituted porphyrinogens (**7e** and **7f**) were oxidized with chloranil, and *meso*-unsubstituted porphyrinogens (**7g** and **7h**) were oxidized with 0.1% aqueous $FeCl_3$ in $CHCl_3$ at room temperature to obtain $16\pi$-conjugated systems **5e** in 6%, **5f** in 7%, **5g** in 5%, and **5h** in 4% yields (Scheme 2).

**Scheme 2. Synthesis of Porphyrinogens (7e−h) and 5,10-Porphodimethenes (5e−h)**




The structures of all the products were characterized by IR, $^1H$ NMR, $^{13}C$ NMR, CHN analysis, and mass spectrometry (see the Supporting Information). The $^1H$ NMR spectra of tellurium-embedded porphodimethenes **5b**, **5d**, **5f**, and **5h** were recorded in $CDCl_3$ at room temperature. In general, the $sp^3$-hybridized 5,10-*meso*-tetramethyl protons ($CH_3$) resonate as a doublet at $\delta$ 1.78−1.75, while conjugated tellurophene protons are more deshielded and appeared as a sharp singlet at $\delta$ 7.60−7.62 compared to the nonconjugated tellurophene protons ($\delta$ 7.59−7.47). On the other hand, in the $^1H$ NMR spectra of selenium-embedded porphodimethenes **5a**, **5c**, **5e**, and **5g**, 5,10-*meso* tetramethyl proton ($CH_3$) resonate as a sharp singlet at $\delta$ 1.77 while conjugated and nonconjugated selenophene protons appeared at $\delta$ 7.07 and 6.91, respectively. The $sp^2$ *meso*-CH protons of **5g** and **5h** resonate as a sharp singlet in the range of $\delta$ 6.73−6.71. The difference in $sp^3$-hybridized 5,10-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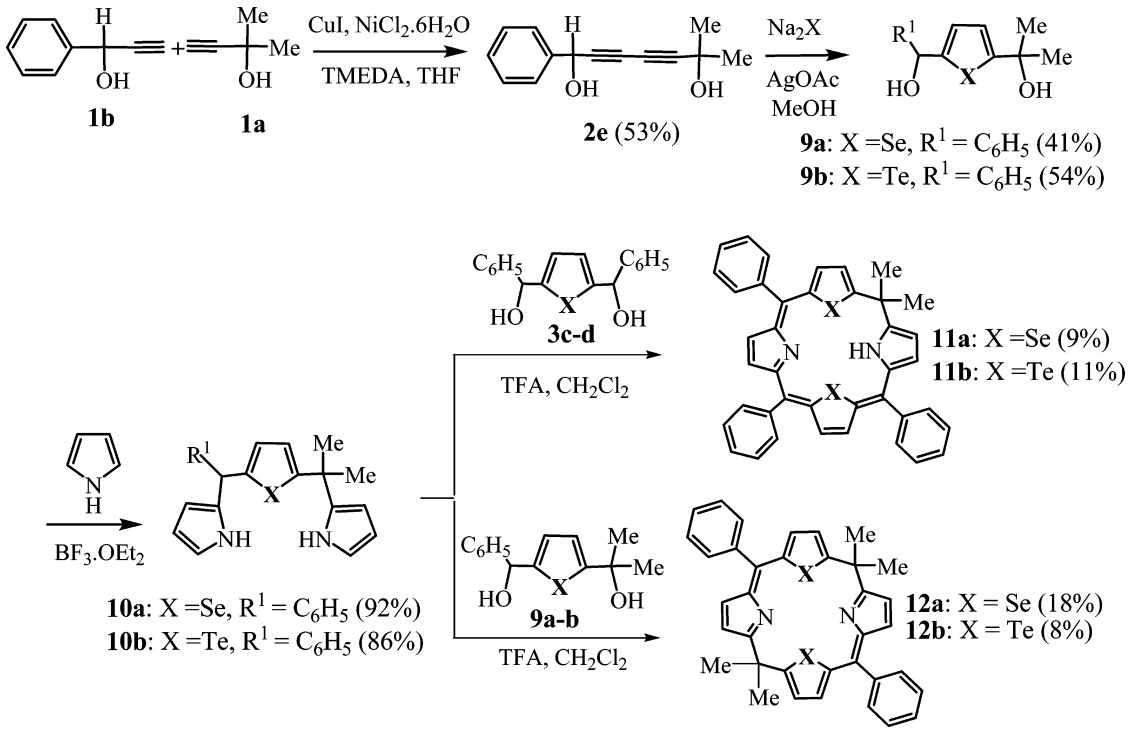
**Scheme 3. Synthesis of 5,15-Porphodimethenes (12a and 12b) and Porphotrimethenes (11a and 11b)**




*meso* tetramethyl chemical shifts and the splitting pattern between Te and Se calixphyrins reflects the difference in the degree of distortion in their conformation; this may be ascribed to the difference in sizes of Se/Te incorporated in their $\pi$-conjugated **N-X-N** subunits. The UV−vis absorption spectra of Se hybrids **5a**, **5c**, **5e** and **5g** showed the transitions at lower wavelengths at around 343 and 520 nm. For Te hybrids **5b**, **5d**, **5f**, and **5h** in $CH_2Cl_2$, broad absorptions due to $\pi-\pi^*$ transitions were observed around 561−559 nm along with an intense band around 360−358 nm (Supporting Information). Unsubstituted 15,20-*meso*-carbon porphodimethenes (**5g** and **5h**) are highly unstable and very difficult to handle and become dark at room temperature in comparison to 15,20-*meso*-substituted porphodimethene.

The cross coupling of haloalkyne with a terminal alkyne catalyzed by Cu(I) is the most important method for the synthesis of unsymmetrical diynes (Scheme 3).[24] Although the nickel-catalyzed oxidative coupling reaction of two different terminal alkynes using $O_2$ as the oxidant at room temperature has been reported for the facile synthesis of unsymmetrical diynes,[21] the symmetrical diynes are also formed and separated from the reaction mixture. The reaction of 1 equiv of unsymmetrical diols (**9a**) with 1 equiv of corresponding 16-selenatripyrranes (**4a**) in dichloromethane (method A) gave porphomethenes **6a** in 9% yield (Scheme 1). Similarly, ditelluraporphomethene (**6b**) was obtained in 7% yield. The absorption spectra of ditelluraporphomethene (564 and 360 nm) and diselenaporphomethene (440 and 328 nm) were quite similar to the absorption spectra of ditellura/diselenaporpho-dimethene. In the $^1$H NMR spectra of selenaporphomethene (**6a**), the four $\beta$-pyrrole protons appeared as two sets of multiplets in the range of $\delta$ 6.0−6.3, and two different $\beta$-selenophene protons appeared as a multiplet and a singlet at $\delta$ 6.9 and 7.1, respectively (Supporting Information).

The reaction of unsymmetrical 16-selenatripyrrane (**10a**) and symmetrical selenophene diols (**3c**) in dichloromethane, in the presence of a catalytic amount of trifluoroacetic acid at room temperature, followed by oxidation with DDQ gave the porphotrimethene (**11a**) in 9% yield. The presence of a strong $M^+$ ion peak in the mass spectra and correct elemental analysis confirmed the synthesis of phlorin (**11a**). Similarly, the other porphotrimethene **11b** was synthesized in 11% yield and characterized by IR, NMR, and UV−vis spectroscopy. Phlorins **11a** and **11b** are quite stable under nitrogen and isolable (Scheme 3).

The $^1$H NMR data of **11b** are typical for a nonaromatic conjugated system with four sets of signals of four $\beta$-pyrrole protons in the range of $\delta$ 6.3−7.1 as compared to the 21,23-ditelluraporphyrins.[18c,d] The four $\beta$-tellurophene protons appeared as two sets of signals: a doublet at $\delta$ 7.5 and a multiplet at $\delta$ 7.6. The inner NH proton showed two broad signals at $\delta$ 11.2 and 12.2 that were attributed tentatively to the presence of tautomers in solution. However, when the $^1$H NMR spectrum was recorded using deuterated pyridine ($C_5D_5N$) as a solvent, only one broad signal at $\delta$ 10.2 was observed, which disappeared upon addition of a drop of $D_2O$ (exchange of the NH proton with a deuterium atom), confirming the NH signal. The tautomeric effect of the inner NH proton has been previously reported with 21,23-dithiaphlorins.[17i]

Generally, the electronic absorption spectra of phlorins displayed absorption at a wavelength longer than that of porphyrins.[17,18c,d] The electronic absorption spectra of diselenaphlorin **11a** showed absorption bands at 679 and 438 nm, whereas ditelluraphlorin (**11b**) showed a pattern different from that of 21,23-dithia/diselenaphlorins and appeared as a broad Q-band at 583 nm and a Soret band at 362 nm. The change in conformation due to the presence of tellurium had been previously reported with 21,23-ditelluraporphyrin;[18b]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21,23-ditelluraporphyrin has been shown to adapt a nonplanar macrocyclic conformation, and its chromophore is found to be different from regular heteroporphyrins.[18b]

The reaction of unsymmetrical 16-selenatripyrrane (**10a**) with unsymmetrical selenophene diols (**9a**) in dichloromethane, in the presence of trifluoroacetic acid (1.5h), followed by DDQ oxidation gave the newer 5,15-porphodimethene (**12a**). The newer 5,15-porphodimethene (**12a**) was characterized by UV−vis, $^1$H NMR, and correct elemental analysis. The $^1$H NMR spectra of both the compounds are in good agreement for the given structure. Similarly, the other 5,15-porphodimethene (**12b**) was synthesized (Scheme 3). The electronic absorption spectrum of 5,15-diselenaporphodimethene **12a** is quite different from that of 5,10-diselenaporphodimethene **5a**. The UV−vis spectrum of **5a** showed two sharp peaks at 343 and 520 nm, whereas in the UV−vis spectrum of **12a**, a broad peak at 426 nm along with a shoulder at 525 nm was observed. It is quite understandable due to the presence of conjugated double bonds in diselenaporphodimethene **5a**. Compared to those of 5,10-porphodimethene (**5a**), the $^1$H NMR spectra of 5,15-porphodimethene (**12a**) showed a different pattern. The selenophene protons appeared as two sets of doublets at 7.52 and 7.35 ppm, whereas the $\beta$-pyrrolic proton appeared at 6.83 and 6.22 ppm as doublets. Similarly, porphodimethene (**12b**) showed a broad absorption spectrum at 443 and 536 nm. Porphodimethene (**12b**) readily undergoes decomposition in air.

The problematic role of mercury for the environment has necessitated the investigation of the detection of mercury with suitable chemosensors.[25] The chalcogenophilicity of mercury led to the development of various sensors from compounds containing chalcogen atoms. Chalcogen−mercury binding is stronger than chalcogen−zinc or chalcogen−magnesium binding because of the strong relativistic 6s orbital contraction that draws the chalcogen charge to the $Hg^{2+}$ nucleus.[25] The greater stability of phenyl-substituted calixphyrin among those of other calixphyrins offers the further utilization of these compounds in the selective detection of mercury. The electronic absorption spectroscopic titration of 5,10-porphodimethene **5a** with a "soft" Lewis acid, mercuric perchlorate $Hg(ClO_4)_2$, was performed in an acetonitrile/water mixture [6:4 (v/v)] at room temperature. Calixphyrin **5a** gave characteristic absorption maxima at 339 and 514 nm, and upon addition of $Hg^{2+}$ in an acetonitrile/water solution [6:4 (v/v)] of **5a** (1:1 complex), the absorption peak was bathochromically shifted to 415 and 584 nm (shifted by 70 nm) with the increase in relative intensity (Figure 2). The bright red solution of **5a** turned gray upon complexation with $Hg^{2+}$, and the color changes were clearly visible to the naked eye. The binding constant for the formation of the 1:1 complex from the interaction of **5a** and $Hg^{2+}$ was calculated from the plot of $1/(A - A_0)$ versus $1/[Hg^{2+}]$ using the Benesi−Hildebrand equation[26] and was found to be $1.37 \times 10^7$ $M^{-1}$. The linearity of the plot further confirmed the 1:1 binding stoichiometry. The UV−vis absorption response of **5a** was also examined in the presence of 1−100 equiv of various metal ions such as $K^+$, $Ag^+$, $Mn^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Cr^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ in an acetonitrile/water solution [6:4 (v/v)] (Supporting Information). No significant changes in UV−vis intensity were observed with these metal ions, which indicated the selective chelation of $Hg^{2+}$ with **5a** (Figure S15 of the Supporting Information).

The fluorescence spectroscopic titration of **5a** with $Hg^{2+}$ was performed in an acetonitrile/water solution [6:4 (v/v)] at room temperature. Compound **5a** showed characteristic emission peaks at 404 and 430 nm upon excitation at 350 nm. The fluorescence was gradually quenched upon the stepwise addition of $Hg^{2+}$ (from 0.5 to 5.0 $\mu$m) to a solution of **5a** (2 $\mu$m) (Figure 3). The fluorescence quenching upon addition of $Hg^{2+}$ was attributed to the formation of a complex between **5a** and $Hg^{2+}$.[27] The fluorescence response of **5a** was also examined in the presence of 1−100 equiv of various metal ions such as $K^+$, $Ag^+$, $Mn^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Cr^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ in an acetonitrile/water solution [6:4 (v/v)] (Figure S16 of the Supporting Information). No significant changes in fluorescence intensity were observed with these metal ions, whereas the significant quenching of fluorescence intensity was observed with 1 equiv of $Hg^{2+}$. Hence, selective chelation of $Hg^{2+}$ with **5a** was observed.

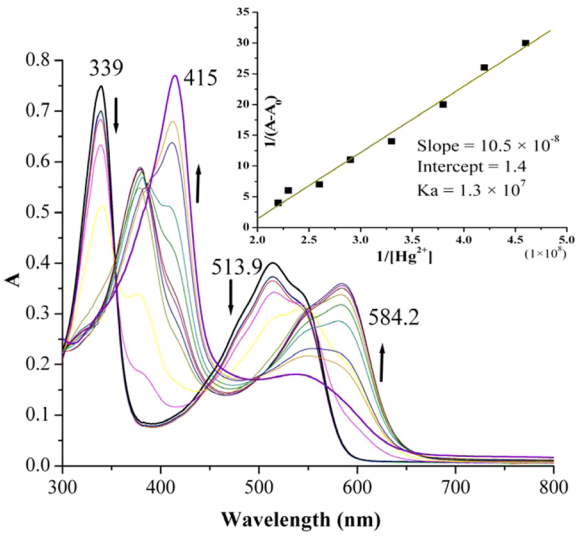


**Figure 2.** UV−vis titration profile of **5a** ($5.1 \times 10^{-8}$ M) with the gradual addition of $Hg^{2+}$ in an acetonitrile/water solution [6:4 (v/v)]. The inset shows the Benesis−Hildebrand plot of **5a**, assuming a 1:1 stoichiometry for association between **5a** and $Hg^{2+}$.

The electronic absorption spectroscopic titration of **5b** with $Hg^{2+}$ was also performed, and their respective preliminary peaks were shifted by 18−20 nm. The binding constant was calculated to be $3 \times 10^6$ $M^{-1}$ (Figure 4). The detection limits of **5a** and **5b** were calculated for $Hg^{2+}$ ions, and we found that **5a** ($1.1 \times 10^{-7}$ M) showed a detection limit higher than that of **5b** ($3.2 \times 10^{-6}$ M) (Figures S19 and S20 of the Supporting Information). Similar studies were conducted with 5,15-porphodimethenes **12a** and **12b**, but no significant changes were observed (Figures S20 and S21 of the Supporting Information).

The $^1$H NMR spectrum of selenium calixphyrin with $Hg^{2+}$ at 298 K was recorded (Figure 5 and Table S1 of the Supporting Information). A significant downfield chemical shift change was observed for selenophene protons (conjugated and unconjugated) and pyrrolic protons of **5a**. **5a** exhibited conjugated and unconjugated selenophene protons at 7.07 and 6.91 ppm, respectively, and pyrrolic protons at 6.67−6.71 ppm that were significantly downfield shifted to 7.45, 7.26, and 6.71−6.74 ppm, respectively. This finding suggests the interaction takes place through the selenium of selenophene (conjugated and unconjugated) and nitrogen of the pyrrole ring of **5a**. Similar changes in chemical shifts were also observed in calixphyrin **5b** in which $Hg^{2+}$ binds with tellurium of tellurophene (conjugated


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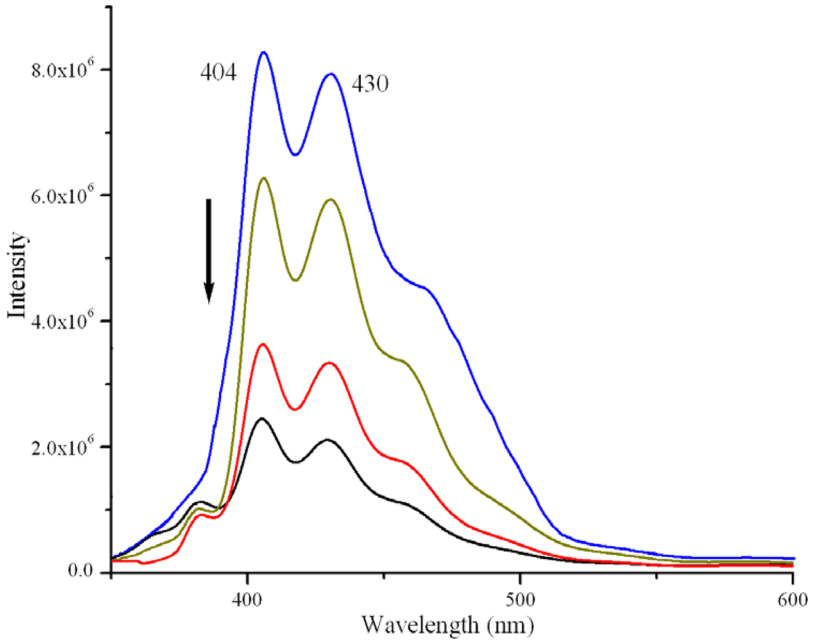


**Figure 3.** Changes in the fluorescence spectra ($\lambda_{ex}$ = 350 nm) of **5a** (10 $\mu$M) measured upon addition of $Hg^{2+}$.

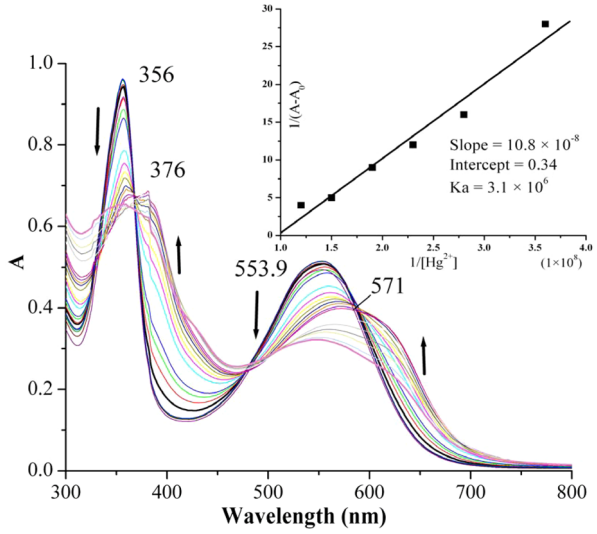


**Figure 4.** UV–vis titration profile of **5b** ($4.8 \times 10^{-8}$ M) with the gradual addition of $Hg^{2+}$ in an acetonitrile/water solution [6:4 (v/v)]. The inset shows the Benesis–Hildebrand plot of **5b**, assuming a 1:1 stoichiometry for association between **5b** and $Hg^{2+}$.

and unconjugated) and the nitrogen of the pyrrole (Figure S63 of the Supporting Information). The higher binding constant for mercury with selenium calix[4]phyrins than with tellurium calix[4]phyrins has been observed by UV–vis spectroscopy. Stronger inhibition of fluorescence is observed in the case of different selenium calix[4]phyrins than in the case of tellurium calix[4]phyrins.

The titration profile of **11a** ($6 \times 10^{-7}$ M) with $Hg^{2+}$ was recorded in an acetonitrile/water solution [6:4 (v/v)] (Figure 6). Upon addition of $Hg^{2+}$, the intensity of the absorption peak at 679 nm decreased and a gradual red shift in the spectral position at 826 nm was observed, along with an increase in the absorption intensity; the binding constant was calculated to be $2.3 \times 10^4$ $M^{-1}$. In the $^1H$ NMR spectra of **11a** with $Hg^{2+}$, the tautomeric effect of the inner NH proton was restricted because of the presence of $Hg^{2+}$ in solution and inner NH proton appeared at $\delta$ 10.3, and significant downfield chemical shift changes in selenophene protons and pyrrolic protons were observed (Figure S64 of the Supporting Information). Titration of **6a** with 1 equiv of $Hg^{2+}$ resulted in a small decrease in the absorption at 328 and 440 nm with a 60 nm bathochromic shift (Figure 7), and the binding constant was calculated to be 16.1 $\times 10^4$ $M^{-1}$. The lower binding constants for the interaction of $Hg^{2+}$ with porphomethene **6a** and porphotrimethene **11a** compared to the binding constant for the interaction with porphodimethenes **5a** and **12a** suggest the difference in macrocycle flexibility and conjugation and the presence of NH pyrrolic units in **6a** and **11a** as compared to porphodimethenes.

## CONCLUSIONS

In conclusion, the first syntheses of 21,23-diselena/ditellura core-modified porphomethenes, 5,10-porphodimethenes, 5,15-porphodimethenes, and porphotrimethenes (phlorins) have been achieved from easily available precursors. The reaction approach using readily available conjugated diynes as starting materials makes this strategy highly attractive in diversity-oriented synthesis. The different selenium-substituted calix[4]-phyrins are more stable than tellurium-substituted calix[4]-phyrins, and these calixphyrins have shown better selectivity for $Hg^{2+}$. The binding ability of calixphyrins with $Hg^{2+}$ ion has been examined by using $^1H$ NMR, UV–vis, and fluorescence spectroscopy.

## EXPERIMENTAL SECTION

**General Experimental Details.** Melting points were determined on a capillary melting point apparatus and are uncorrected. The chemical shifts ($\delta$) are referenced to the respective solvents, and splitting patterns are designed as s (singlet), d (doublet), t (triplet), m (multiplet), dt (double triplet), br (broad), and brs (broad singlet). Coupling constants ($J$) are reported in hertz. The mass spectra of selected compounds were recorded on an Agilent Technologies high-resolution Q-TOF mass spectrometry instrument. Solvents used were of analytical grade and were dried before being used. Pyrrole was


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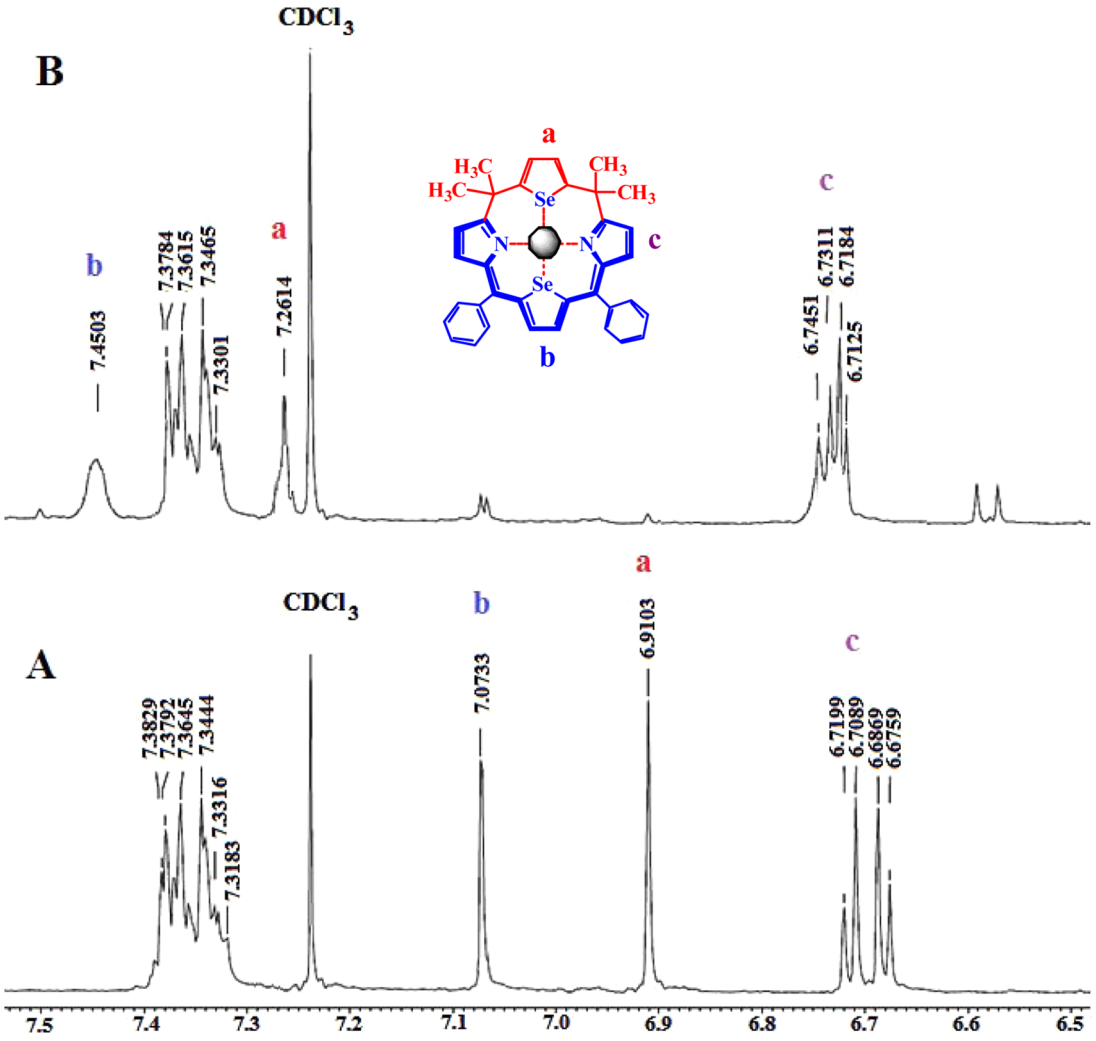


**Figure 5.** $^{1}$H NMR spectrum of **5a** with $Hg^{2+}$. (A) **5a** (from 6.5 to 7.5 ppm). (B) **5a** with $Hg^{2+}$ (1 equiv) in $CDCl_3$.

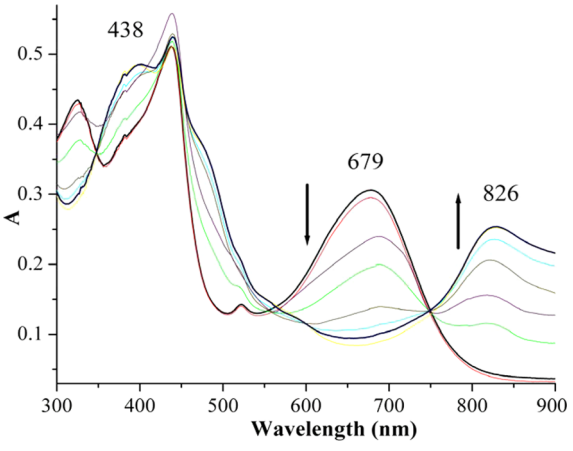


**Figure 6.** UV−vis titration profile of **11a** ($6 \times 10^{-7}$ M) with the gradual addition of $Hg^{2+}$ in an acetonitrile/water solution [6:4 (v/v)].

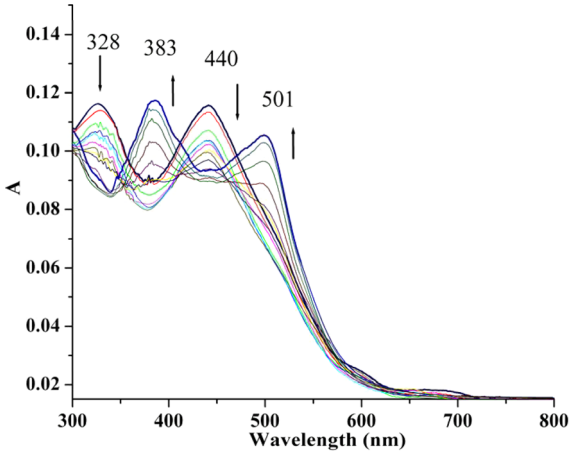


**Figure 7.** UV−vis titration profile of **6a** ($3.1 \times 10^{-8}$ M) with the gradual addition of $Hg^{2+}$ in an acetonitrile/water solution [6:4 (v/v)].

distilled before being used. All other chemicals were purchased as reagent quality and used as received. All processes and reactions were conducted under argon and protected from light.

**Synthesis of Symmetrical Diynediols (2a−d).** The symmetrical diynediols (**2a−d**) were synthesized by slightly modifying our reported procedure.[20]

**Synthesis of Unsymmetrical Diynediols (2e).** The diynediols (**2e**) were synthesized by slightly modifying the literature procedure.[21] The solution of TMEDA (46.4 mg, 0.4 mmol), CuI (19.05 mg, 0.1 mmol), and $NiCl_2{\cdot}6H_2O$ (23.78 mg, 0.1 mmol) in THF (10 mL) was stirred at room temperature. A THF (10 mL) solution of 2-methylbut-3-yn-2-ol **1a** (252 mg, 3 mmol) and alkynes (**1b**) (264 mg, 2 mmol) were added dropwise with the bubbling of oxygen to the reaction



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mixture. The reaction was monitored by TLC. After completion of the reaction (10 h), the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel. The product was eluted with a benzene/acetone solution [97.5:2.5 (v/v)] to give unsymmetrical diynediols as a pale yellow liquid.

*6-Methyl-1-phenylhepta-2,4-diyne-1,6-diol (**2e**).*[28] Yellow liquid (227 mg, 53%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.49 (d, 2H, $C_6H_5$), 7.37 (m, 3H, $C_6H_5$), 5.50 (s, 1H, CH), 2.37 (brs, 1H, OH), 2.05 (brs, 1H, OH), 1.53 [s (split), 6H, $CH_3$].

**Reaction of Diynediols (2a−d or 8) with Selenium and Tellurium: Synthesis of Symmetrical and Unsymmetrical Selenophene and Tellurophene Diols (3a−h, 9a, and 9b).** A 250 mL three-neck flask equipped with a nitrogen inlet, a reflux condenser, and a dropping funnel was loaded with selenium/tellurium (4 mmol), $NaBH_4$ (16 mmol), and distilled water (10 mL). The reaction mixture was vigorously stirred under nitrogen for 30 min. A deoxygenated solution of diynediols (**2a−d** or **8**) (3.1 mmol) in MeOH (12 mL) with AgOAc (50 mg) was added dropwise, and the reaction mixture was stirred overnight.[2] After completion of the reaction, water (100 mL) was added and the product was extracted with a benzene/diethyl ether mixture (1:1, 150 mL). The organic layer was washed with water (2 × 20 mL) and dried over anhydrous $Na_2SO_4$, and the solvent was evaporated under reduced pressure to give products (**3a−h**, **9a**, and **9b**) as an off-white solid (83−94%). All symmetrical selenophene and tellurophene diols (**3a−h**) were characterized, and their values matched the reported values.[20]

*2-{5-[Hydroxy(phenyl)methyl]selenophen-2-yl}propan-2-ol (**9a**).* Yellow liquid (375 mg, 41%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44−7.28 (m, 5H, $C_6H_5$), 6.86 (m, 2H, selenophene), 5.94 (s, 1H, CH), 2.49 (brs, 1H, OH), 1.59 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 161.9, 153.8, 143.4, 128.5, 127.9, 126.3, 126.1, 123.0, 74.2, 72.8, 32.2, 30.9. HRMS (ESI-QTOF): $[M + H]^+$ calcd for $C_{14}H_{17}O_2Se$ $m/z$ 297.0394, found $m/z$ 297.0391. CHN analysis. Calcd for $C_{14}H_{16}O_2Se$: C, 56.95; H, 5.46. Found: C, 56.99; H, 5.52.

*2-{5-[Hydroxy(phenyl)methyl]tellurophen-2-yl}propan-2-ol (**9b**).* Yellow liquid (576 mg, 54%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.43 (m, 2H, tellurophene), 7.33−7.20 (m, 5H, $C_6H_5$), 5.77 (s, 1H, CH), 2.77 (brs, 1H, OH), 2.34 (brs, 1H, OH), 1.58 [s (split), 6H, $CH_3$]. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 165.7, 156.6, 146.2, 135.6, 132.0, 130.6, 129.9, 128.0, 78.7, 34.3, 34.2. HRMS (ESI-QTOF): $[M + H]^+$ calcd for $C_{14}H_{17}O_2Te$ $m/z$ 347.0291, found $m/z$ 347.0298. CHN analysis. Calcd for $C_{14}H_{16}O_2Te$: C, 48.90; H, 4.69. Found: C, 48.96; H, 4.78.

**Reaction of Tellurophene and Selenophene Diols (3a and 3b, respectively) with Pyrrole: Synthesis of Symmetrical Selenatripyrrane (4a) and Telluratripyrrane (4b).** Boron trifluoride-etherate (0.3 mmol) was added to the solution of diols (**3a** and **3b**) (0.7 mmol) in degassed pyrrole (6.5 mL), and the resulting mixture was stirred for 1 h under argon. The reaction was monitored by TLC. After completion of the reaction, it was diluted with $CH_2Cl_2$ (30 mL) and 40% NaOH (25 mL). The organic layer was separated and washed with water (3 × 100 mL) and brine (100 mL). It was dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified over silica gel (80:20 hexanes/EtOAc) to give 78−91% of **4a** and **4b** as a white solid.

*5,5,10,10-Tetramethyl-16-selenatripyrromethane (**4a**).*[20] White solid (181 mg, 75% yield). Mp: 97 °C. $R_f$ = 0.2 [8:2 (v/v) petroleum/EtOAc]. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.91 (br, 2H, NH), 6.71 (s, 2H, selenophene), 6.65 (m, 2H, pyrrole), 6.12−6.05 (m, 4H, pyrrole), 1.69 (s, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 160.94, 139.68, 124.10, 116.78, 107.72, 103.54, 39.68, 31.61. IR (KBr) $\nu_{max}$: 3372, 3099, 2967, 1559, 1439, 1383, 1312, 1296, 1231, 1112, 1036, 949, 803, 722, 583 cm$^{-1}$. HRMS (ESI-QTOF): $[M + H]^+$ calcd for $C_{18}H_{23}N_2Se$ $m/z$ 347.1026, found $m/z$ 347.1050. CHN analysis. Calcd for $C_{18}H_{22}N_2Se$: C, 62.60; H, 6.42; N, 8.11. Found: C, 62.57; H, 6.22; N, 8.41.

*5,5,10,10-Tetramethyl-16-telluratripyrromethane (**4b**).*[20] White solid (215 mg, 78% yield). Mp: 148 °C. $R_f$ = 0.2 [8:2 (v/v) petroleum/EtOAc]. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.93 (br, 2H, NH), 7.10 (s, 2H, tellurophene), 6.65 (m, 2H, pyrrole), 6.10−6.03 (m, 4H, pyrrole), 1.66 (s, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.41, 140.73, 131.27, 116.91, 107.71, 103.35, 42.04, 31.92. IR (KBr) $\nu_{max}$: 3367, 2964, 2861, 1559, 1381, 1361, 1254, 1236, 1112, 1037, 1010, 965, 807, 723, 581 cm$^{-1}$. HRMS (ESI-QTOF): $[M + H]^+$ calcd for $C_{18}H_{23}N_2Te$ $m/z$ 397.0923, found $m/z$ 397.0912. CHN analysis. Calcd for $C_{18}H_{22}N_2Te$: C, 54.87; H, 5.63; N, 7.11. Found: C, 54.70; H, 5.82; N, 7.28.

**Reaction of Selenophene and Tellurophene Diols (9a and 9b, respectively) with Pyrrole: Synthesis of Unsymmetrical Selenatripyrrane and Telluratripyrrane (10a and 10b, respectively).** Boron trifluoride-etherate (0.3 mmol) was added to the solution of diols (**9a** and **9b**) (0.7 mmol) in degassed pyrrole (6.5 mL), and the resulting mixture was stirred for 1 h under argon. The reaction was monitored by TLC. After completion of the reaction, it was diluted with $CH_2Cl_2$ (30 mL) and 40% NaOH (25 mL). The organic layer was separated and washed with water (3 × 100 mL) and brine (100 mL). It was dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified over silica gel (80:20 hexanes/EtOAc) to give 78−91% of **10a** and **10b** as a yellow oil.

*10,10-Dimethyl-5-phenyl-16-selenatripyrromethane (**10a**).* Yellow oil (253 mg, 92% yield). $R_f$ = 0.3 [8:2 (v/v) petroleum/EtOAc]. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.91 (br, 2H, NH), 7.27 (m, 5H, Ph), 6.73 (s, 2H, selenophene), 6.66 (m, 2H, pyrrole), 6.12−5.92 (m, 4H, pyrrole), 5.55 (s, 1H, CH), 1.67 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.1, 152.2, 143.1, 139.6, 133.3, 128.5, 1287.3, 127.2, 124.3, 117.1, 116.8, 108.3, 107.7, 107.4, 103.5, 48.1, 39.7, 31.6, 30.9, 29.6. HRMS (ESI-QTOF): $[M + H]^+$ calcd for $C_{18}H_{23}N_2Se$ $m/z$ 395.1026, found $m/z$ 395.1042. CHN analysis. Calcd for $C_{22}H_{22}N_2Se$: C, 67.17; H, 5.64; N, 7.12. Found: C, 67.16; H, 5.38; N, 7.51.

*10,10-Dimethyl-5-phenyl-16-telluratripyrromethane (**10b**).* Yellow oil (266 mg, 86%). $R_f$ = 0.3 [8:2 (v/v) petroleum/EtOAc]. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.93 (br, 2H, NH), 7.28−7.27 (m, 4H, Ph), 7.24−7.14 (dd, 2H, tellurophene), 6.65−6.63 (m, 2H, pyrrole), 6.12−6.07 (m, 4H, pyrrole), 5.44 (s, 1H, CH), 1.65 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 151.42, 143.71, 138.6, 132.21, 132.01, 128.2, 127.6, 126.8, 125.3, 124.3, 116.11, 115.8, 107.81, 103.35, 41.04, 39.01, 32.32. IR (KBr) $\nu_{max}$: 3351, 3332, 2901, 2853, 1563, 1389, 1322, 1262, 1202, 1108, 1007, 952, 821, 752 cm$^{-1}$. HRMS (ESI-QTOF): $[M + H]^+$ calcd for $C_{22}H_{23}N_2Te$ $m/z$ 445.0923, found $m/z$ 445.0928. CHN analysis. Calcd for $C_{22}H_{22}N_2Te$: C, 59.78; H, 5.02; N, 6.34. Found: C, 59.62; H, 5.12; N, 6.48.

**Reaction of Selenophene and Tellurophene Diols (3c and 3d, respectively) with Selena- and Telluratripyrromethane (4a and 4b, respectively): Synthesis of 5,10-Porphodimethene 5a−d (method A).** To a degassed solution of tripyrrane (**4a** and **4b**) (0.50 mmol) and selenophene and tellurophene diols (**3c** and **3d**, respectively) (0.50 mmol) in $CH_2Cl_2$ (250 mL), $BF_3{\cdot}OEt_2$ (0.091 mmol) was added dropwise and the reaction mixture was stirred for 1 h at room temperature, followed by oxidation with 2.2 equiv of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone). After 1 h, the solvent was evaporated under reduced pressure to give a black crude mixture. The crude was purified by column chromatography on silica gel using $CH_2Cl_2$ as an eluent to afford solid **5a−d** (9−11%).

*5,5,10,10-Tetramethyl-15,20-bis(phenyl)-21,23-diselenaporphodimethene (**5a**).* Orange solid (32.40 mg, 10% yield). Mp: 173 °C dec. $R_f$ = 0.5 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 339, 514 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.38−7.31 (m, 10H, $C_6H_5$), 7.07 (s, 2H, selenophene), 6.91 (s, 2H, selenophene), 6.71−6.67 (dd, 4H, pyrrole), 1.78 (s, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 182.7, 158.7, 158.1, 152.5. 144.8, 137.1, 136.6, 135.3, 130.3, 128.3, 127.6, 125.9, 124.9, 43.0, 29.6, 23.3. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{36}H_{30}N_2Se_2$ $m/z$ 650.073, found $m/z$ 650.079.

*5,5,10,10-Tetramethyl-15,20-bis(phenyl)-21,23-ditelluraporphodimethene (**5b**).* Purple solid (11 mg, 11% yield). Mp: 191 °C dec. $R_f$ = 0.4 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 356, 554 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.60 (s, 2H, tellurophene), 7.59 (s, 2H, tellurophene) 7.37−7.33 (m, 10H, Ph), 6.69 (s, 4H, pyrrole), 1.78−1.75 (d, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 181.8, 161.2, 158.4, 152.6, 150.5, 143.5, 136.6, 135.9, 134.7, 130.2, 128.2, 137.6, 125.4, 45.1, 34.0, 29.6. 26.6, 22.9. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{36}H_{30}N_2Te_2$ $m/z$ 750.053, found $m/z$ 750.051.



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*5,5,10,10-Tetramethyl-15,20-bis(phenyl)-21-selena-23-telluraporphodimethene (**5c**).* Orange solid (31 mg, 9%). Mp: 178 °C dec. $R_f$ = 0.5 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 343, 520, 554 nm. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 2H, tellurophene), 7.38−7.34 (m, 10H, Ph), 6.89 (s, 2H, selenophene), 6.71−6.65 (dd, 4H, pyrrole), 1.79−1.74 (d, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 183.3, 158.2, 152.6, 144.6, 136.8, 135.3, 132.9, 130.3, 128.2, 127.6, 125.9, 45.0, 29.6. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{36}H_{30}N_2SeTe$ *m/z* 700.063, found *m/z* 700.065.

*5,5,10,10-Tetramethyl-15,20-bis(phenyl)-21-selena-23-telluraporphodimethene (**5d**).* Purple solid (42 mg, 12%). Mp: 189 °C dec. $R_f$ = 0.5 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 359, 560 nm. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 2H, tellurophene), 7.37−7.21 (m, 10H, Ph), 7.18 (s, 2H, selenophene), 6.71−6.68 (m, 4H, pyrrole), 1.78 (d, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 181.2, 161.9, 158.0, 152.6, 150.7, 143.4, 136.4, 134.7, 130.2, 128.2, 128.0, 127.6, 125.3, 43.1, 31.1, 27.7. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{36}H_{30}N_2SeTe$ *m/z* 700.063, found *m/z* 700.061.

**Reaction of Selenophene and Tellurophene Diols (3e and 3f, respectively) with Selena- and Telluratripyrromethane (4a and 4b, respectively): Synthesis of 5,10-Porphodimethene 5e and 5f (method B, isolation of porphyrinogens 7e and 7f and oxidation with *p*-chloranil).** The methanolic solution (5 mL) of diol (**3e** and **3f**) (2 mmol) was added to a degassed solution of tripyrrane (**4a** and **4b**) (2 mmol) in $CH_2Cl_2$ (200 mL). The reaction was conducted at 0 °C in a dark room under argon. After 20 min, a 20% $BF_3{\cdot}CH_3OH$ solution (0.4 mmol) was added with a micropipette and the reaction mixture was stirred for 1 h at 0 °C. The stirring was continued at room temperature for 1 h. After completion of the reaction, the solvent was evaporated under reduced pressure and a viscous colorless oil was obtained, which was purified by column chromatography on silica gel using $CH_2Cl_2$ as an eluent to afford porphyrinogen (**7e** and **7f**) as a colorless solid in 12−14% yield. Further, the isolated porphyrinogens were subjected to oxidation.

*5,5,10,10,15,20-Hexamethyl-21,23-diselenaporphyrinogen (**7e**).* White solid (127 mg, 12%). Mp: 169 °C dec. $R_f$ = 0.5 [8:2 (v/v) petroleum/$CHCl_3$]. IR (KBr) $\nu_{max}$: 3351, 2854, 2821, 1584, 1352, 1198, 969, 796 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.26 (br, 2H, H, stereoisomer), 7.28 (br, H, NH, stereoisomer), 6.83 (s, H, selenophene, stereoisomer), 6.86−6.85 (m, H, selenophene, stereoisomer), 6.86−6.88 (m, H, selenophene, stereoisomer), 5.87 (m, H, pyrrole, stereoisomer), 5.86 (m, H, pyrrole, stereoisomer), 4.17 (m, 4H, CH, stereoisomer), 4.16 (m, H, CH, stereoisomer), 1.54 (s, H, $CH_3$, stereoisomer), 1.56 (s, H, $CH_3$, stereoisomer). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 163.01, 157.5, 157.3, 156.4, 155.3, 143.87, 136.2, 136.1, 131.89, 124.6, 124.4, 103.6, 103.2, 103.1, 102.05, 41.36, 37.0, 36.9, 36.5, 22.5, 22.3, 22.2. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{26}H_{30}N_2Se_2$ *m/z* 530.073, found *m/z* 530.071.

*5,5,10,10,15,20-Hexamethyl-21,23-ditelluraporphyrinogen (**7f**).* White solid (175 mg, 14%). Mp: 153 °C dec. $R_f$ = 0.5 [8:2 (v/v) petroleum/$CHCl_3$]. IR (KBr) $\nu_{max}$: 3438, 2941, 2868, 1581, 1391, 1101, 984, 751 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.31 (br, 2H, NH), 7.249 (m, 2H, tellurophene), 7.240 (m, 2H, tellurophene, isomer), 7.231 (m, 2H, tellurophene), 7.230 (m, 2H, tellurophene, isomer), 5.85−5.83 (*m*, 4H, pyrrole), 5.82−5.80 (m, 4H, pyrrole, isomer), 4.11−4.07 (q, 1H, CH), 4.00−3.95 (q, 1H, CH) 1.63−1.61 (d, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 163.2, 163.1, 159.0, 157.4, 141.9, 137.6, 137.2, 131.4, 131.1, 130.4, 130.3, 102.6, 102.0, 101.4, 101.3, 42.2, 40.4, 40.0 33.3, 31.2, 30.8, 28.8, 235, 21.9. HRMS (Q-TOF): *m/z* 630.051 ($M^+$). HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{26}H_{30}N_2Te_2$ *m/z* 630.053, found *m/z* 630.051.

To a degassed solution of porphyrinogen (**7e** and **7f**) (1 mmol) in $CHCl_3$ (10 mL) was added *p*-chloranil at room temperature, and the mixture was stirred for 10 min. The organic solvent was evaporated under reduced pressure and purified by column chromatography on silica gel using a petroleum/$CHCl_3$ mixture as an eluent to afford solid product **5e** and **5f** in 6−7% yield.

*5,5,10,10,15,20-Hexamethyl-21,23-diselenaporphodimethene (**5e**).* Brick solid (31.50 mg, 6% yield). $R_f$ = 0.45 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 349, 529 nm. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 2H, selenophene), 6.91 (s, 2H, selenophene), 6.72−6.67 (m, 4H, pyrrole), 3.63 (s, 6H, 15,20-*meso*-$CH_3$), 1.77 (s, 12H, $CH_3$). HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{26}H_{26}N_2Se_2$ *m/z* 526.043, found *m/z* 526.044.

*5,5,10,10,15,20-Hexamethyl-21,23-ditelluraporphodimethene (**5f**).* Purple solid (43.50 mg, 7% yield). $R_f$ = 0.5 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 350, 544 nm. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2H, tellurophene), 7.56 (s, 2H, tellurophene), 6.70−6.62 (m, 4H, pyrrole), 3.69 (s, 6H, 15,20-*meso*-$CH_3$), 1.78−1.76 (d, 12H, $CH_3$). HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{26}H_{26}N_2Te_2$ *m/z* 626.022, found *m/z* 626.021.

**Reaction of Selenophene and Tellurophene Diols (3g and 3h, respectively) with Selena and Telluratripyrromethane (4a and 4b, respectively): Synthesis of 5,10-Porphodimethene (5g and 5h) (method B, isolation of porphyrinogens 7g and 7h and oxidation with a 0.1% aqueous $FeCl_3$ solution).** To a degassed solution of tripyrranes (**4a** and **4b**) (1.8 mmol) in $CH_2Cl_2$ (200 mL) was added the methanolic solution (4.2 mL) of diols (**3g** and **3h**) (1.8 mmol). The reaction was conducted at 0 °C in a dark room under argon. After 20 min, a 20% $BF_3{\cdot}CH_3OH$ solution (0.38 mmol) was added with a micropipette and the reaction mixture was stirred for 1 h. Stirring was continued for 1 h at room temperature. After completion of the reaction, the solvent was evaporated under reduced pressure to give a viscous colorless soild. The solid was purified by column chromatography on silica gel using a petroleum/$CHCl_3$ mixture as an eluent to afford porphyrinogens (**7g** and **7h**) as a colorless solid in 10−11% yield.

*5,5,10,10-Tetramethyl-15,20-tetrahydro-21,23-diselenaporphyrinogen (**7g**).* White solid (99 mg, 11%). Mp: 149 °C dec. $R_f$ = 0.4 [8:2 (v/v) petroleum/$CHCl_3$]. IR (KBr) $\nu_{max}$: 3441, 2941, 1682, 1432, 1381, 1233, 1054, 798, 754, 705, 563 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.28 (br, 2H, NH), 6.84 (s, 2H, selenophene), 6.82 (s, 2H, selenophene), 5.86−5.85 (m, 4H, pyrrole), 4.02 (s, 4H, $CH_2$), 1.63 (s, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 162.74, 151.4, 143.89, 131.02, 130.54, 128.01, 105.64, 102.00, 41.22, 31.79, 31.6. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{24}H_{26}N_2Se_2$ *m/z* 502.042, found *m/z* 502.044.

*5,5,10,10-Tetramethyl-15,20-tetrahydro-21,23-ditelluraporphyrinogen (**7h**).* White solid (107.50 mg, 10%). Mp: 158 °C dec. $R_f$ = 0.4 [8:2 (v/v) petroleum/$CHCl_3$]. IR (KBr) $\nu_{max}$: 3442, 2957, 2915, 1641, 1422, 1355, 1215, 1041, 788, 741, 723, 591 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.33 (br, 2H, NH), 7.24 (s, 2H, tellurophene), 7.22 (s, 2H, tellurophene), 5.82−5.80 (*m*, 4H, pyrrole), 3.96 (s, 4H, $CH_2$), 1.63 (s, 12H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 162.6, 150.6, 143.9, 131.1, 130.9, 106.4, 102, 41.2, 32.8. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{24}H_{26}N_2Te_2$ *m/z* 602.022, found *m/z* 602.017.

The isolated porphyrinogens were subjected to oxidation. To a degassed solution of porphyrinogen (**7g** and **7h**) (1 mmol) in $CHCl_3$ (10 mL) was added a 0.1% aqueous $FeCl_3$ solution at room temperature, and the mixture was stirred for 10 min. The organic solvent was separated and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel using a petroleum/$CHCl_3$ mixture as an eluent to obtain solid **5g** and **5h** in 4−5% yield.

*5,5,10,10-Tetramethyl-21,23-diselenaporphodimethene (**5g**).* Red solid (25 mg, 5%). Mp: 134 °C dec. $R_f$ = 0.6 [5:5 (v/v) petroleum/$CHCl_3$]. IR (KBr) $\nu_{max}$: 2864, 2851 2811, 1531, 1351, 1321, 1184, 1031, 951, 781 $cm^{-1}$. UV−vis ($CHCl_3$): 331, 528 nm. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.103 (s, 2H, selenophene), 6.91 (s, 2H, selenophene), 6.71 (s, 2H, 15,20-*meso*-H), 6.67−6.70 (m, 4H, pyrrole), 1.87 (s, 12H, $CH_3$). HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{24}H_{22}N_2Se_2$ *m/z* 498.011, found *m/z* 498.011.

*5,10-Tetramethyl-21,23-ditelluraporphodimethene (**5h**).* Purple solid (24 mg, 4%). Mp: 139 °C dec. $R_f$ = 0.7 [5:5 (v/v) petroleum/$CHCl_3$]. IR (KBr) $\nu_{max}$: 2882, 2841 2801, 1504, 1366, 1358, 1154, 1051, 961, 796 $cm^{-1}$. UV−vis ($CHCl_3$): 346, 554 nm. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 2H, tellurophene), 7.32 (s, 2H, tellurophene), 6.73 (s, 2H, 15,20-*meso*-H), 6.69−6.67 (m, 4H, pyrrole), 1.78−1.76 (d, 12H, $CH_3$). HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{24}H_{22}N_2Te_2$ *m/z* 597.991, found *m/z* 597.994.



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**Reaction of Selenophene and Tellurophene Diols (9a and 9b, respectively) with Selena- and Telluratripyrromethane (4a and 4b, respectively): Synthesis of Porphomethene 6a and 6b.** To a degassed solution of selena- and telluratripyrrane (**4a** and **4b**, respectively) ($3 \times 10^{-4}$ mol) in DCM (200 mL) were added selenophene and tellurophene diols (**9a** and **9b**, respectively) ($3 \times 10^{-4}$ mol), and the reaction was started by the dropwise addition of a catalytic amount of trifluoroacetic acid (0.020 mL) for 90 min, under a nitrogen atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, DDQ ($3 \times 10^{-4}$ mol) was added and the stirring was continued in air for 10 min. The crude mixture was purified by silica gel column chromatography, and the separated product was characterized as **6a** and **6b** in 7−9% yield.

*5,5,10,10,15,15-Hexamethyl-20-phenyl-21,23-diselenaporphomethene (**6a**).* Brown solid (16 mg, 9%). $R_f$ = 0.6 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 328, 440 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.85 (brs, 1H, NH), 7.37−7.33 (m, 5H, Ph), 7.04 (m, 2H, selenophene), 6.93 (s, 2H, selenophene), 6.31 (m, 2H, pyrrole), 6.03 (d, 2H, $J$ = 4.2, pyrrole), 1.74 (s, 6H, $CH_3$), 1.66 (d, 12H, $CH_3$). CHN analysis. Calcd for $C_{32}H_{32}N_2Se_2$: C, 63.79; H, 5.35; N, 4.65. Found: C, 63.93; H, 5.22; N, 4.21.

*5,5,10,10,15,15-Hexamethyl-20-phenyl-21,23-ditelluraporphomethene (**6b**).* Dark purple solid (15 mg, 7%). $R_f$ = 0.6 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 360, 564 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.01 (brs, 1H, NH), 7.62 (m, 2H, tellurophene), 7.50 (s, 2H, tellurophene), 7.37−7.33 (m, 5H, Ph), 6.35 (m, 2H, pyrrole), 6.02 (m, 2H, $J$ = 4.2, pyrrole), 1.72−1.64 (m, 18H, $CH_3$). HRMS (Q-TOF): $m/z$ 704.215 ($M^+$). HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{32}H_{32}N_2Te_2$ $m/z$ 704.211, found $m/z$ 704.213. CHN analysis. Calcd for $C_{32}H_{32}N_2Te_2$: C, 54.92; H, 4.61; N, 4.00. Found: C, 54.93; H, 5.02; N, 4.11.

**Reaction of Selenophene and Tellurophene Diols (3c and 3d, respectively) with Selena- and Telluratripyrromethane (10a and 10b, respectively): Synthesis of Porphotrimethene 11a and 11b.** The selenophene and tellurophene diols (**3c** and **3d**, respectively) ($3 \times 10^{-4}$ mol) and selena- and telluratripyrrane (**10a** and **10b**, respectively) ($3 \times 10^{-4}$ mol) were condensed in 250 mL of $CH_2Cl_2$ under nitrogen in the presence of a catalytic amount of trifluoroacetic acid (0.020 mL) for 2 h under an inert atmosphere. DDQ ($3 \times 10^{-4}$ mol) was added, and stirring was continued in air for an additional 1 h. The crude mixture was purified by silica gel column chromatography, and the desired **11a** and **11b** were collected as a green solid (9−11%).

*5,5′-Dimethyl-10,15,20-triphenyl-21,23-diselenaporphotrimethene (**11a**).* Green solid (19 mg, 9%). $R_f$ = 0.6 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 438, 679 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 12.73 (br s, 1H, NH), 11.32 (br s, 1H, NH), 7.53−7.11 (m, 19H, Ph and $\beta$-selenophene), 7.11 (br s, 1H, $\beta$-pyrrole), 6.90 (d, 1H, $\beta$-pyrrole), 6.67 (d, 1H, $\beta$-pyrrole), 6.28 (d, 1H, $\beta$-pyrrole), 1.91 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 180.1, 179.2, 170.6. 159.3, 155.8, 150.2, 145.7, 137.5 134.2, 132.9, 132.1, 132.0, 131.1, 129.1, 128.6, 122.2, 45.8, 32.1, 31.9. HRMS (ESI-QTOF): $[M + H]^+$ calcd for $C_{40}H_{31}N_2Se_2$ $m/z$ 699.0818, found $m/z$ 699.0748. CHN analysis. Calcd for $C_{40}H_{30}N_2Se_2$: C, 68.97; H, 4.34; N, 4.02. Found: C, 69.03; H, 4.31; N, 4.03.

*5,5′-Dimethyl-10,15,20-triphenyl-21,23-ditelluraporphotrimethene (**11b**).* Green solid (26 mg, 11%). $R_f$ = 0.6 [5:5 (v/v) petroleum/$CHCl_3$]. UV−vis ($CHCl_3$): 362, 583 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 12.20 (br s, 1H, NH), 11.20 (br s, 1H, NH), 7.64 (m, 3H, $\beta$-tellurophene), 7.53 (d, 1H, $\beta$-tellurophene), 7.43−7.20 (m, 15H, Ph), 7.11 (d, 1H, $\beta$-pyrrole), 6.91 (d, 1H, $\beta$-pyrrole), 6.66 (d, 1H, $\beta$-pyrrole), 6.25 (d, 1H, $\beta$-pyrrole), 1.93 (s, 6H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 180.6, 179.3, 178.8. 158.4, 155.6, 151.2, 146.5, 136.6, 134.9, 132.7, 132.2, 130.6, 128.6, 128.2,122.4, 45.1, 34.6, 34.5. HRMS (ESI-QTOF): $[M]^+$ calcd for $C_{40}H_{30}N_2Te_2$ $m/z$ 798.052, found $m/z$ 798.054. CHN analysis. Calcd for $C_{40}H_{30}N_2Te_2$: C, 60.52; H, 3.81; N, 3.53. Found: C, 60.61; H, 3.96; N, 3.63.

**Reaction of Selenophene and Tellurophene Diols (9a and 9b, respectively) with Selena- and Telluratripyrromethane (10a and 10b, respectively): Synthesis of Porphodimethene 12a and 12b.** To a degassed solution of selena- and telluratripyrrane (**10a** and **10b**, respectively) ($3 \times 10^{-4}$ mol) in DCM (200 mL) were added selenophene and tellurophene diols (**9a** and **9b**, respectively) ($3 \times 10^{-4}$ mol), and the reaction was started by the dropwise addition of a catalytic amount of trifluoroacetic acid (0.020 mL) for 2 h under a nitrogen atmosphere. The progress of the reaction was monitored by TLC. After consumption of the starting material, DDQ ($3 \times 10^{-4}$ mol) was added and stirring was continued in air for 10 min. The crude mixture was purified by silica gel column chromatography, and the separated red solid product was characterized as **12a** and **12b** (12−18%).

*5,5,15,15-Tetramethyl-10,20-diphenyl-21,23-diselenaporphodimethene (**12a**).* Red solid (35 mg, 18%). UV−vis ($CH_2Cl_2$): 426, 525 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.52 (d, 2H, $\beta$-selenophene), 7.35 (d, 2H, $\beta$-selenophene), 7.06−7.28 (m, 10H, $C_6H_5$), 6.83 (d, 2H, $\beta$-pyrrole), 6.22 (d, 2H, $\beta$-pyrrole), 1.21 (s, 12H, $CH_3$). CHN analysis. Calcd for $C_{36}H_{30}N_2Se_2$: C, 66.67; H, 4.66; N, 4.32. Found: C, 66.46; H, 4.42; N, 4.28.

*5,5,15,15-Tetramethyl-10,20-diphenyl-21,23-ditelluraporphodimethene (**12b**).* Red solid (18 mg, 8%). UV−vis ($CH_2Cl_2$): 443, 536 nm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.81 (d, 2H, $\beta$-tellurophene), 7.74 (d, 2H, $\beta$-tellurophene), 7.08−7.26 (m, 10H, $C_6H_5$), 6.85 (d, 2H, $\beta$-pyrrole), 6.26 (d, 2H, $\beta$-pyrrole), 1.23 (s, 12H, $CH_3$). CHN analysis. Calcd for $C_{36}H_{30}N_2Te_2$: C, 57.97; H, 4.05; N, 3.76. Found: C, 57.84; H, 4.18; N, 3.86.

**General Procedure for the Sensing of $Hg^{2+}$ with Calixphyrins.** All the experiments were conducted at an ambient temperature of 25 °C. For every experiment, a fresh solution was prepared. The solution of calixphyrins in acetonitrile (2 mL) was taken in a spectrophotometer cuvette, and the absorption spectrum was recorded. A 20 $\mu$L stock solution of $Hg(ClO_4)_2$ with a similar concentration was added to the cuvette and mixed well, and the absorption spectrum was recorded. Similarly, a mercury solution was added to the cuvette until the absorption spectrum began to change. In addition, the binding constant was calculated by using the Benesi−Hilderbrand equation.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1$H NMR, $^{13}$C NMR, HRMS, and UV−vis spectra of all new compounds and UV−vis and fluorescence spectra of $Hg^{2+}$ titration with newer calix[4]phyrins. 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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## ■ REFERENCES

(1) (a) Sessler, J. L.; Zimmerman, R. S.; Bucher, C.; Kral, V.; Andrioletti, B. *Pure Appl. Chem.* **2001**, *73*, 1041. (b) Woodward, R. B. *Angew. Chem.* **1960**, *72*, 651. (c) Woodward, R. B.; Ayer, W. A.; Beaton, J. M.; Bickelhaupt, F.; Bonnett, R.; Buchschacher, P.; Closs, G. L.; Dutler, H.; Hannah, J.; Hauck, F. P.; Ito, S.; Langemann, A.; LeGoff, E.; Leimgruber, W.; Lwowski, W.; Sauer, J.; Valenta, Z.; Voltz, H. *J. Am. Chem. Soc.* **1960**, *82*, 3800.

(2) (a) Bucher, C.; Seidel, D.; Lynch, V.; Kral, V.; Sessler, J. L. *Org. Lett.* **2000**, *2*, 3103. (b) Bernatkova, M.; Andrioletti, B.; Kral, V.; Rose, E.; Vaissermann, J. *J. Org. Chem.* **2004**, *69*, 8140.



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J. Org. Chem. XXXX, XXX, XXX−XXX

(3) (a) Pistner, A. J.; Lutterman, D. A.; Ghidiu, M. J.; Ma, Y.-Z.; Rosenthal, J. *J. Am. Chem. Soc.* **2013**, *135*, 6601. (b) Bruce, A. M.; Weyburne, E. S.; Engle, J. T.; Ziegler, C. J.; Geier, G. R. *J. Org. Chem.* **2014**, *79*, 5664.
(4) (a) Karthik, G.; Krushna, P. V.; Srinivasan, A.; Chandrashekar, T. K. *J. Org. Chem.* **2013**, *78*, 8496. (b) Salini, P. S.; Thomas, A. P.; Sabarinathan, R.; Ramakrishnan, S.; Sreedevi, K. C. G.; Reddy, M. L. P.; Srinivasan, A. *Chem.—Eur. J.* **2011**, *17*, 6598.
(5) (a) Sessler, J. L.; Camiolo, S.; Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 17. (b) Chang, K. C.; Minami, T.; Koutnik, P.; Savechenkov, P. Y.; Liu, Y.; Anzenbacher, P., Jr. *J. Am. Chem. Soc.* **2014**, *136*, 1520. (c) Finnigan, E. M.; Giordani, S.; Senge, M. O.; McCabe, T. *J. Phys. Chem. A* **2010**, *114*, 2464. (d) Jha, S. C.; Lorch, M.; Lewis, R. A.; Archibald, S. J.; Boyle, R. W. *Org. Biomol. Chem.* **2007**, *5*, 1970.
(6) (a) Holaday, M. G. D.; Tarafdar, G.; Kumar, A.; Reddy, M. L. P.; Srinivasan, A. *Dalton Trans.* **2014**, *43*, 7699. (b) Matano, Y.; Fujita, M.; Miyajima, T.; Imahori, H. *Organometallics* **2009**, *28*, 6213. (c) Matano, Y.; Fujita, M.; Miyajima, T.; Imahori, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2010**, *185*, 1098.
(7) Bachmann, J.; Hodgkiss, J. M.; Young, E. R.; Nocera, D. G. *Inorg. Chem.* **2007**, *46*, 607.
(8) Arciero, D. M.; Hooper, A. B. *Biochem. Soc. Trans.* **1998**, *26*, 385.
(9) (a) Burns, D. H.; Shi, D. C.; Lash, T. D. *Chem. Commun.* **2000**, 299. (b) Lash, T. D.; Gandhi, V. *J. Org. Chem.* **2000**, *65*, 8020.
(10) (a) Yip, K. W.; Zhang, Z.; Nakatsugawa, N. S.; Huang, J. W.; Vu, N. M.; Chiang, Y. K.; Lin, C. L.; Kwan, J. Y. Y.; Yue, S.; Jitkova, Y.; To, T.; Zahedi, P.; Pai, E. F.; Schimmer, A. D.; Lovell, J. F.; Sessler, J. L.; Liu, F. F. *PLoS One* **2014**, *9*, e89889. (b) Phillips, J. D.; Bergonia, H. A.; Reilly, C. A.; Franklin, M. R.; Kushner, J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 5079. (c) Danton, M.; Lim, C. K. *Biomed. Chromatogr.* **2007**, *21*, 661.
(11) Sergeeva, N. N.; Shaker, Y. M.; Finnigam, E. M.; McCabe, T.; Senge, M. O. *Tetrahedron* **2007**, *63*, 12454.
(12) Bonomo, L.; Solari, E.; Scopelliti, R.; Latronico, M.; Floriani, C. *Chem. Commun.* **1999**, 2227.
(13) (a) Serra, A. C.; Gonsalves, A. M. R. *Tetrahedron Lett.* **2010**, *51*, 4192. (b) Nascimento, B. F. O.; Gonsalves, A. M. R.; Pineiro, M. *Inorg. Chem. Commun.* **2010**, *13*, 395.
(14) Bergonia, H. A.; Phillips, J. D.; Kushner, J. P. *Anal. Biochem.* **2009**, *384*, 74.
(15) (a) Dolensky, B.; Kroulik, J.; Kral, V.; Sessler, J. L.; Dvorakova, H.; Bour, P.; Bernatkova, M.; Bucher, C.; Lynch, V. *J. Am. Chem. Soc.* **2004**, *126*, 13714. (b) Pistner, A. J.; Lutterman, D. A.; Ghidiu, M. J.; Walker, E.; Yap, G. P. A.; Rosenthal, J. *J. Phys. Chem. C* **2014**, *118*, 14124. (c) Dehaen, W. *Top. Heterocycl. Chem.* **2010**, *24*, 75.
(16) (a) Matano, Y.; Miyajima, T.; Nakabuchi, T.; Imahori, H.; Ochi, Y.; Sakaki, S. *J. Am. Chem. Soc.* **2006**, *128*, 11760. (b) Ochi, N.; Nakao, Y.; Sato, H.; Matano, Y.; Imahori, H.; Sakaki, S. *J. Am. Chem. Soc.* **2009**, *131*, 10955. (c) Matano, Y.; Imahori, H. *Acc. Chem. Res.* **2009**, *42*, 1193. (d) Matano, Y.; Miyajima, T.; Ochi, N.; Nakao, Y.; Sakaki, S.; Imahori, H. *J. Org. Chem.* **2008**, *73*, 5139. (e) Beyzavi, M. H.; Lentz, D.; Reissig, H. U.; Wiehe, A. *Eur. J. Org. Chem.* **2013**, 269. (f) Ganapathi, E.; Chatterjee, T.; Ravikanth, M. *Dalton Trans.* **2015**, *44*, 2763.
(17) (a) Gupta, I.; Frohlich, R.; Ravikanth, M. *Eur. J. Org. Chem.* **2008**, 1884. (b) Gupta, I.; Frohlich, R.; Ravikanth, M. *Chem. Commun.* **2006**, 3726.
(18) (a) Abe, M.; Detty, M. R.; Gerlits, O. O.; Sukumaran, D. K. *Organometallics* **2004**, *23*, 4513. (b) Pacholska, E.; Grazynski, L. L.; Ciunik, Z. *Angew. Chem., Int. Ed.* **2001**, *40*, 4466. (c) Abe, M.; Hilmey, D. G.; Stilts, C. E.; Sukumaran, D. K.; Detty, M. R. *Organometallics* **2002**, *21*, 2986. (d) Sathyamoorthy, B.; Axelrod, A.; Farwell, V.; Bennett, S. M.; Calitree, B. D.; Benedict, J. B.; Sukumaran, D. K.; Detty, M. R. *Organometallics* **2010**, *29*, 3431.
(19) Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *Tetrahedron Lett.* **1978**, *19*, 167.
(20) Ahmad, S.; Yadav, K. K.; Singh, S. J.; Chauhan, S. M. S. *RSC Adv.* **2014**, *4*, 3171.
(21) (a) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632. (b) Glaser, C. *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422. (c) Glaser, C. *Ann. Chem. Pharm.* **1870**, *154*, 137. (d) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.
(22) (a) Yin, W.; He, C.; Chen, M.; Zhang, H.; Lei, A. *Org. Lett.* **2009**, *11*, 709. (b) Shi, W.; Lei, A. *Tetrahedron Lett.* **2014**, *55*, 2763. (c) Kurita, T.; Abe, M.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Synlett* **2007**, 2521. (d) McCormick, T. M.; Jahnke, A. A.; Lough, A. J.; Seferos, D. S. *J. Am. Chem. Soc.* **2012**, *134*, 3542.
(23) (a) Jang, Y. S.; Kim, H. J.; Lee, P. H.; Lee, C. H. *Tetrahedron Lett.* **2000**, *41*, 2919. (b) Arumugam, N.; Ka, J. W.; Lee, C. H. *Tetrahedron* **2001**, *57*, 7323. (c) Kral, V.; Sessler, J. L.; Zimmerman, R. S.; Seidel, D.; Lynch, V.; Andrioletti, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1055.
(24) (a) Ahammed, S.; Kundu, D.; Ranu, B. C. *J. Org. Chem.* **2014**, *79*, 7391. (b) Peng, H.; Xi, Y.; Ronaghi, N.; Dong, B.; Akhmedov, N. G.; Shi, X. *J. Am. Chem. Soc.* **2014**, *136*, 13174.
(25) (a) Zou, W.; Filatov, M.; Atwood, D.; Cremer, D. *Inorg. Chem.* **2013**, *52*, 2497. (b) Namor, A. F. D. D.; Abbas, I. *J. Phys. Chem. B* **2007**, *111*, 5803. (c) Kumar, A.; Singh, J. D. *Inorg. Chem.* **2012**, *51*, 772. (d) Parthiban, C.; Manivannan, R.; Elango, K. P. *Dalton Trans.* **2015**, *44*, 3259.
(26) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
(27) (a) Tamayo, A.; Lodeiro, C.; Escriche, L.; Casabo, J.; Covelo, B.; Gonzalez, P. *Inorg. Chem.* **2005**, *44*, 8105. (b) Fang, Z.; Pu, K.-Y.; Liu, B. *Macromolecules* **2008**, *41*, 8380.
(28) Wu, W.; Gao, Y.; Jiang, H.; Huang, Y. *J. Org. Chem.* **2013**, *78*, 4580.


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