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Novel 21,23-Ditelluraporphyrins and the First 26,28-Ditellurasapphyrin and 30,33-Ditellurarubyrin

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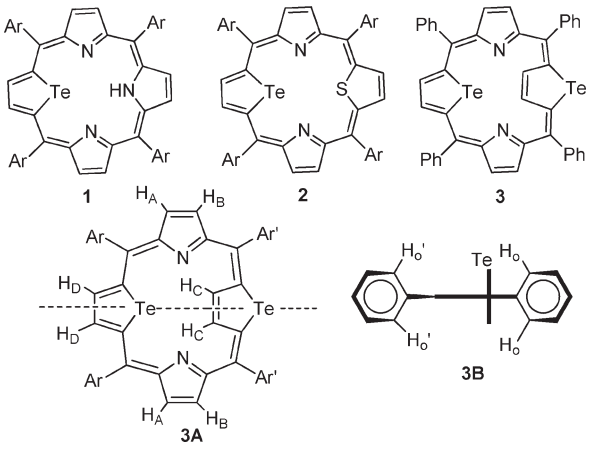
21,23-Ditelluraporphyrins **3**, **9**, and **16**−**18** bearing phenyl, 4-methoxyphenyl, and/or 3,4,5-trimethoxyphenyl *meso* substituents were prepared by the condensation of 2,5-di[hydroxy(aryl)methyl]tellurophenes **12** with 2,5-di[2-pyrrolo(aryl)methyl]tellurophenes **15** in the presence of BF_3−etherate followed by oxidation with *p*-chloranil. Compounds **15** were prepared from tellurophenes **12** with pyrrole and BF_3−etherate. Tellurophenes **12** were prepared in 44−72% isolated yield by the addition of 1,6-diarylhexa-2,4-diyn-1,6-diols **13** to the reduction product of Te powder and $LiBHEt_3$. No additional Lewis acid was necessary in these reactions. Coupling of 1-aryl-2-propyn-1-ols (**14**) with CuCl, pyridine, and air in MeOH gave diyndiols **13**. 26,28-Ditellurasapphyrin **10** was isolated in 0.6% yield from the reaction mixture that produced **9** in 12% isolated yield. The X-ray structure of **10** showed a nearly planar sapphyrin core with the Te atoms of both tellurophene rings pointing to the center of the core. 30,33-Ditellurarubyrin **11** was isolated in 32% yield by the reaction of two equivalents of trifluoroacetic acid with tellurophene dipyrrane **15c**. ^{125}Te NMR spectra were recorded for the compounds of this study.

Core-modified porphyrins replace one or two pyrrole N−H groups with O, S, Se, and/or Te atoms. The tellura- and ditelluraporphyrins provide the broadest range of unusual structures and chemical reactivity. 23-Telluraporphyrin **1** (Chart 1) has a Te···N distance of 3.13 Å, which is less than the sum of van der Waals radii.[1] 21-Thia-23-telluraporphyrin **2** has a Te···S distance of 2.65 Å,[2] which is even more compressed. In 21,23-ditelluraporphyrin **3**, the dominant structure both in solution and in the crystalline state is one in which the two Te atoms cannot both occupy the core and one tellurophene is "flipped" with the Te atom pointed away from the porphyrin core (as represented by **3A** and **3B** in Chart 1).[3] Telluraporphyrins **1** and **2** are easily oxidized,[4] and the close proximity of heteroatoms leads to unusual bonding interactions within the core with Te in the +4 oxidation state.[5] Telluraporphyrins **1** and **2** are also catalysts for the activation of H_2O_2 via oxidation of Te(II) to Te(IV).[6]

Chart 1



The unusual structure of ditelluraporphyrin **3** gives reduced symmetry relative to other porphyrins, and core-modified porphyrins and spectral features of the ditelluraporphyrin are quite different from those of related structures. The "flipped" tellurophene of **3** exchanges positions with the other tellurophene via a dynamic process, which is observed in temperature-dependent ^{1}H NMR spectra of **3**.[3] At 210 K, the exchange process has slowed to the point that the ring protons of the two different tellurophenes are distinct with a 2 ppm difference in chemical shift.[3] Furthermore, the symmetry is unusual for a porphyrin with four identical *meso*-substituents with a single mirror plane, as shown in **3A** (Chart 1), as the only symmetry element.

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(1) Latos-Grażyński, L.; Pacholska, E.; Chmielewski, P. J.; Olmstead, M. M.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2252–2254.
(2) Ulman, A.; Manassen, J.; Frolow, F.; Rabinovich, D. *Tetrahedron Lett.* **1978**, 1885–1886.
(3) Pacholska, E.; Latos-Grażyński, L.; Ciunik, Z. *Angew. Chem., Int. Ed.* **2001**, *40*, 4466–4469.
(4) Abe, M.; Hilmey, D. G.; Stilts, C. E.; Sukumaran, D. K.; Detty, M. R. *Organometallics* **2002**, *21*, 2986–2992.
(5) Abe, M.; Detty, M. R.; Gerlits, O. O.; Sukumaran, D. K. *Organometallics* **2004**, *23*, 4513–4518.
(6) Abe, M.; You, Y.; Detty, M. R. *Organometallics* **2002**, *21*, 4546–4551.

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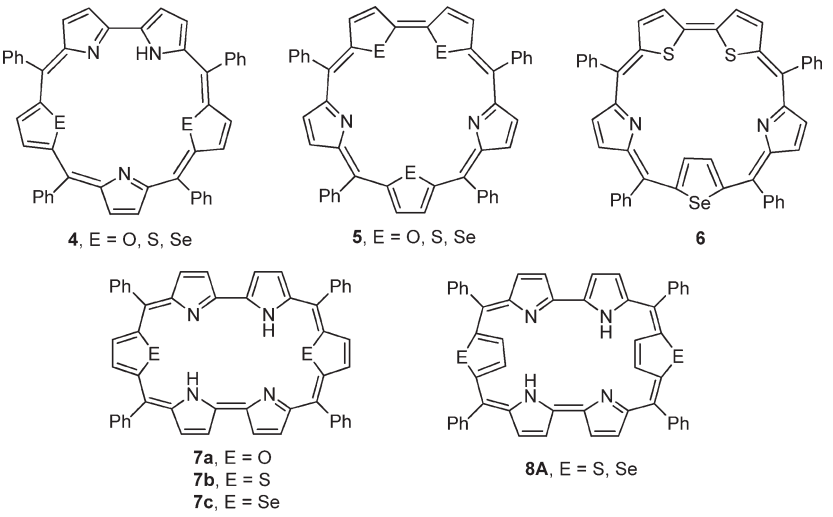
Chart 2

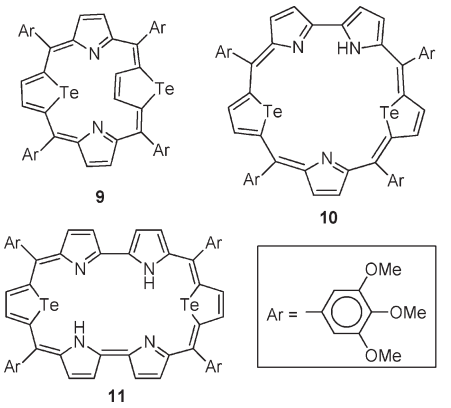


Consequently, the two *ortho*- and *meta*-positions of the *meso*-aryl groups have distinct chemical and magnetic environments, as shown in **3B**.

Expanded porphyrin structures such as the sapphyrins[7] and rubyrins[8] have been described from the traditional Adler synthesis of porphyrins and have been produced in low yields under a variety of reaction conditions.[9] Core-modified sapphyrin analogues of general structures **4**[10,11] and **5**[12] in which pyrrole nitrogen atoms have been replaced with O, S, and Se (Chart 2) have been described. An X-ray structure of selenophene-containing analogue **6**[12b] (Chart 2) shows the same selenophene "inversion" in the solid state as found in the tellurophene "inversion" of ditelluraporphyrin **3**.[3] Tellurophene-substituted sapphyrins might provide some interesting structural variation relative to other analogues.

Core-modified rubyrins **7** (Chart 2) have also been prepared in which two of the rubyrin pyrrole NH groups have been replaced with O, S, and Se atoms.[10a] X-ray structural analysis of crystals of **7b** and **7c** indicate that the thiophene and selenophene rings, respectively, are inverted as in **8A** (Chart 2) with the heteroatoms pointing away from the core, while NMR studies in solution suggest that the predominant solution structure has the heteroatoms pointing toward the core. Again, tellurophene-substituted rubyrins might provide some interesting structural variations relative to other analogues.

Chart 3



Herein, we describe the synthesis of 5,10,15,20-tetrakis-(3,4,5-trimethoxyphenyl)-21,23-ditelluraporphyrin (**9**) and other methoxyaryl-substituted telluraporphyrins. 26,28-Ditellurasapphyrin **10** was isolated as a minor product from the synthesis of **9**, and 30,33-ditellurarubyrin **11** (Chart 3) was prepared independently. Compounds **10** and **11** represent the first reported Te-containing sapphyrin and rubyrin analogues. The methoxy substituents in these molecules should provide precursors to water-soluble analogues, as has been demonstrated for dithia- and diselenaporphyrins, which have been evaluated as photosensitizers[13] and membrane probes.[14]

Results and Discussion

I. Synthesis. 2,5-Di(arylhydroxymethyl)tellurophenes 12 as Precursors to 21,23-Ditelluraporphyrins. The most successful synthetic approaches to telluraporphyrins **1**−**3** are summarized in Scheme 1 and involve 2,5-di(phenylhydroxymethyl)-tellurophene (**12a**) as a key intermediate. Tellurophene **12a** is

(7) (a) Bauer, V. J.; Clive, D. L. J.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429–6436. (b) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perking Trans. 1* **1972**, 2111–2116.

(8) Sessler, J. L.; Morishima, T.; Lynch, V. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 977–980.

(9) (a) Geier, G. R., III; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1596–1603. (b) Geier, G. R., III; Ciringh, Y.; Li, F.; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **2000**, *2*, 1745–1748.

(10) (a) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Vij, A.; Roy, R. *J. Am. Chem. Soc.* **1999**, *121*, 9053–9068. (b) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Vij, A.; Roy, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 3394–3397.

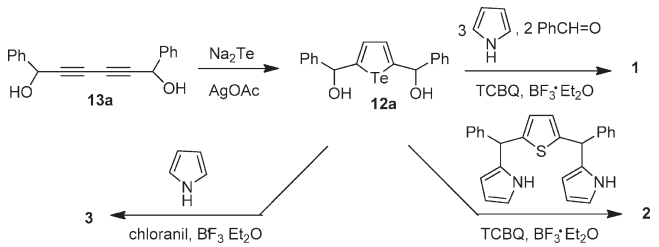
(11) (a) Szterenberg, L.; Latos-Grażyński, L. *J. Phys. Chem. A* **1999**, *103*, 3302–3309. (b) Rachlewicz, K.; Sprutta, N.; Chmielewski, P. J.; Latos-Grażyński, L. *J. Chem. Soc., Perkin Trans. 2* **1998**, 969–976.

(12) (a) Srinivasan, A.; Pushpan, S.; Kumar, M. R.; Mahajan, S.; Chandrashekar, T. K.; Roy, R.; Ramamurthy, P. *J. Chem. Soc., Perkin Trans. 2* **1999**, 961–968. (b) Srinivasan, A.; Anand, V. G.; Narayanan, S. J.; Pushpan, S.; Kumar, M. R.; Chandrashekar, T. K. *J. Org. Chem.* **1999**, *64*, 8693–8697.

(13) (a) Detty, M. R.; Gibson, S. L.; Wagner, S. *J. Med. Chem.* **2004**, *47*, 3897–3915. (b) Hilmey, D. G.; Abe, M.; Nelen, M. I.; Stilts, C. E.; Baker, G. A.; Baker, S. N.; Bright, F. V.; Davies, S. R.; Gollnick, S. O.; Oseroff, A. R.; Gibson, S. L.; Hilf, R.; Detty, M. R. *J. Med. Chem.* **2002**, *45*, 449–461.

(14) Minnes, R.; Weitman, H.; You, Y.; Detty, M. R.; Ehrenberg, B. *J. Phys. Chem. B* **2008**, *112*, 3268–3276.

Scheme 1



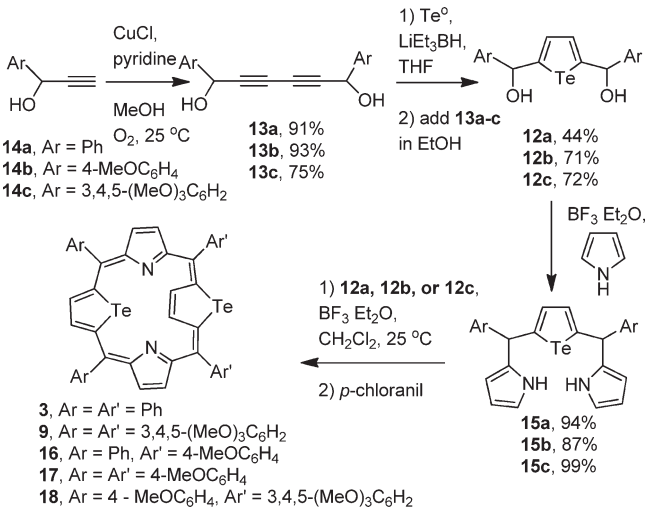
prepared from the corresponding hexa-2,4-diyn-1,5-diol **13a**.[2] Other 2,5-di(1-hydroxy-1-arylmethyl)tellurophenes related in structure to **12a** have not been described.

We examined a general synthesis of 2,5-di(arylhydroxymethyl)-tellurophenes **12** as shown in Scheme 2. The formal addition of H_2Te across 2,4-diyn-1,6-diols **13** leads directly to tellurophenes **12**. Diynediols **13** have been prepared by the oxidative coupling of 1-aryl-1-hydroxy-2-propynes **14** following numerous procedures.[15−19] Compounds **14**, in turn, have been prepared by the addition of magnesium acetylides to aryl aldehydes.[20] Several of the reported methods[15−17] for coupling alkynols **14** were examined, but diyndiols **13** were isolated in only 10−35% yields. The most successful coupling procedure employed was a modification[18] of the Hay coupling[19] of terminal alkynes using catalytic Cu(I) and oxygen as the reoxidant. Diyndiols **13a−c** were isolated in 91%, 93%, and 75% isolated yields from **14a−c**, respectively, using 0.15 equiv of CuCl and 0.3 equiv of pyridine in MeOH under aerobic conditions (Scheme 2).

2,5-Di(1-hydroxy-1-arylmethyl)tellurophenes **12** were prepared by the addition of diyndiols **13** in EtOH to Li_2Te prepared by the reduction of Te powder with 2 equiv of $LiBHEt_3$ in THF (Scheme 2). Tellurophenes **12a−c** were isolated in 44%, 71%, and 72% yields, respectively. The addition of Na_2Te (from $NaBH_4$ and Te powder) across hexadiyndiol **13a** (Scheme 1) gave **12a** in 15% yield and required the presence of the Lewis acid AgOAc.[2] In the absence of AgOAc, the reaction of Na_2Te with **13a** does not give isolable yields of **12a**. However, using Li_2Te prepared from $LiHBEt_3$, no additional Lewis acid catalyst was necessary. The BEt_3 present in the reaction mixture was apparently sufficient as a Lewis acid for the formation of tellurophenes **12** from diynols **13**.

The diyndiols **13** and the tellurophene diols **12** have two chiral centers, and these materials can form racemic mixtures of two diastereomers. The ^1H and ^{13}C NMR spectra of diynols **13** and tellurophene **12a** do not differentiate the two diastereomers. In contrast, tellurophene diols **12b** and **12c** show nearly 1:1 mixtures of the two diastereomers in both the ^1H and ^{13}C NMR spectra of these compounds (Supporting Information). The presence of both diastereomers in **12b** and **12c** suggests that the NMR spectra of the two diastereomers fortuitously overlap in the spectra of diyndiols **13** and tellurophene diol **12a** rather than having only one diastereomer present.

Scheme 2



Synthesis of 21,23-Ditelluraporphyrins 3, 9, and 16−18. Ditelluraporphyrin **3** was isolated in only 11% yield from the Ulman[2] synthesis utilizing **12a**, pyrrole, BF_3−etherate, and chloranil.[3] We examined the [3+1] approach utilizing 1 equiv of **12** and the corresponding tellurophene dipyrrane **15** to prepare 21,23-ditelluraporphyrins.[1,2] Telluorphene diols **12a−c** gave dipyrranes **15a−c** in 94%, 87%, and 99% isolated yields, respectively, upon reaction with pyrrole in the presence of BF_3−etherate (Scheme 2). The ^1H and ^{13}C NMR spectra of dipyrranes **15a−c** suggest either a single diastereomer or, more likely, that the two possible diastereomers of **15a−c** are not differentiated by our conditions for NMR spectroscopy.

Ditelluraporphyrins **3**, **9**, and **16−18** were prepared by the condensation of tellurophene diols **12** with the appropriate dipyrranotellurophene **15** with BF_3 etherate in CH_2Cl_2 followed by oxidation with *p*-chloranil (Scheme 2). Tetraphenyl analogue **3** was isolated in 34% yield following reaction of **12a** and **15a**, which is higher than the 11% yield previously reported.[3] As the number of methoxy substituents on the *meso* aryl groups increased, the yield of ditelluraporphyrin decreased: **16**, with two 4-methoxyphenyl *meso*-substituents, was isolated in 28% yield from reaction of **12b** and **15a**; **17**, with four 4-methoxyphenyl groups, was isolated in 19% yield from reaction of **12b** and **15b**; **18**, with two 4-methoxyphenyl and two 3,4,5-trimethoxyphenyl groups, was isolated in 13% yield from reaction of **12b** and **13c**; and **9**, with four 3,4,5-trimethoxyphenyl groups, was isolated in 12% yield from reaction of **12c** and **13c**.

The ditelluraporphyrins **9** and **16−18** appeared to be stable in the crystalline form. However, in $CHCl_3$ or $CDCl_3$ solution, the ditelluraporphyrins were slowly air oxidized to unknown products.

A second product was isolated from the reaction mixture that produced **9**. 26,28-Ditellurasapphyrin **10** (Chart 2) was isolated in 0.6% yield as a dark purple powder from the reaction of **12c** and **13c** in the presence of BF_3−etherate and chloranil.

Synthesis of 30,33-Ditellurarubyrin 11. Dipyrrane **15c** was treated with 2 equiv of trifluoroacetic acid followed by oxidation with *p*-chloranil[10a] to give 30,33-ditellurarubyrin **11** (Chart 3) in 32% isolated yield after neutralization with Et_3N. Ditellurarubyrin **11** was not formed in any appreciable yield under the reaction conditions used to prepare **9** and **10**,

(15) Chodkiewicz, W.; Cadiot, P. *Compt. Rend.* **1955**, *241*, 1055–1057.
(16) Eglington, G.; Galbraith, A. R. *Chem. Ind.* **1936**, 737–738.
(17) Lei, A. W.; Srivastava, M.; Zhang, X. M. *J. Org. Chem.* **2002**, *67*, 1969–1971.
(18) Stansbury, H. A., Jr.; Proops, W. R. *J. Org. Chem.* **1962**, *27*, 320.
(19) (a) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275–1276. (b) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321.
(20) Bagley, M. C.; Dale, J. W.; Ohnesorge, M.; Xiong, X.; Bower, J. *J. Comb. Chem.* **2005**, *5*, 41–44.

Table 1. Tellurium-125 NMR Chemical Shifts and Absorption Maxima for 21-Telluraporphyrins 1 and 2, 21,23-Ditelluraporphyrins 3, 9, and 16−18, 26,28-Ditellurasapphyrin 10, and 30,33-Ditellurarubyrin 11

compound	^{125}Te NMR, δ[a]	λ_{max}, nm (ε, M^{-1} cm^{-1})[b]
1	833[c]	657 (6400), 628 (5500), 534 (11 200), 482 (sh), 438 (76 000)[c,d]
2	1039[c]	686 (3700), 626 (4200), 545 (sh), 505 (sh), 445 (71 600)[c,d]
3		668 (16 000), 464 (32 000), 348 (25,000)[d,e]
9	731.0	692 (18 600), 489 (43 700), 385 (34 000)
16	730.1	690 (18 200), 484 (38 000), 385 (29 500)
17	729.0	698 (16 300), 484 (37 000), 385 (26 600)
18	726.7	694 (18 100), 488 (38 000), 385 (27 600)
10	731, 1095	830 (17 000), 746 (5200), 668 (18 000), 624 (19v000), 584 (11 000), 512 (190 000)
11	685	982 (73 000), 865 (7900), 750 (66 000), 692 (35 000), 641 (19 000), 548 (520 000)

[a] In $CDCl_3$at 253 K with δ = 0.0 for $^{125}TeMe_2$. [b] In $CHCl_3$. [c] Ref 4. [d] In CH_2Cl_2. [e] ref 3.

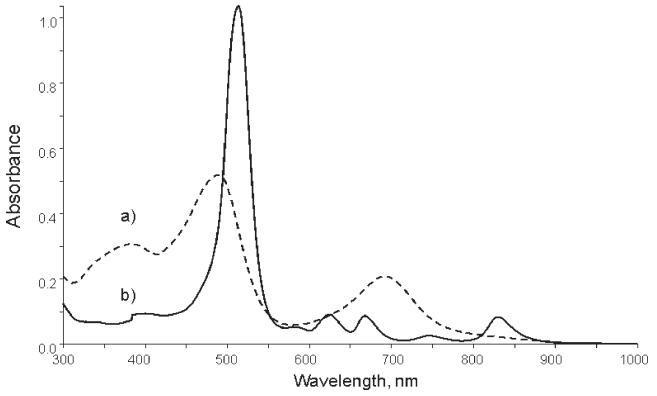


Figure 1. Electronic spectra of (a) 21,23-ditelluraporphyrin **9** (dashed line, 1.2×10^{-5} M) and (b) 26,28-ditellurasapphyrin **10** (solid line, 6.3×10^{-6} M) in $CHCl_3$.

although trace amounts of **11** may have been formed, but in ≤0.05% yield by ^{1}H NMR spectroscopy.

II. Characterization of 21,23-Ditelluraporphyrins 9 and 16−18. Electronic Spectra. The electronic spectra of ditelluraporphyrins **9** and **16−18** were recorded in $CHCl_3$, and maxima are reported in Table 1. Three major bands were observed as illustrated in Figure 1 for ditelluraporphyrin **9** at 385, 489, and 692 nm. The electronic spectra in $CHCl_3$ were red-shifted 18−34 nm relative to the values reported for **3** in CH_2Cl_2 (Table 1).[3] While the three bands were comparable in intensity, the middle band was most intense in all five ditelluraporphyrins. Noticeably absent was the strong Soret−like band observed in telluraporphyrin **1** at 438 nm (ε of 76 000 M^{-1} cm^{-1}) and telluraporphyrin **2** at 445 nm (ε of 71 600 M^{-1} cm^{-1}, Table 1). The 690−698 nm band in the 21,23-ditelluraporphyrins is much stronger than band 1 for telluraporphyrins **1** and **2** and for other 21,23-dithia-, 21-thia-23-selena-, and 21,23-diselenaporphyrins.[13b]

^{125}Te NMR Spectra. As shown in Figure 2, the ^{125}Te NMR spectra of **9** and **16−18** displayed a single ^{125}Te resonance at −20 °C, suggesting that interconversion of "normal" and "flipped" tellurophenes was sufficiently rapid at −20 °C to give an averaged ^{125}Te signal. However, at +20 °C, the ^{125}Te resonance was broadened in ditelluraporphyrins **17** and **18** and was not detectable in ditelluraporphyrins **9** and **16**. These data are consistent with an exchange process involving more than two conformations, which has been previously suggested for the dynamic ^{1}H NMR spectra of ditelluraporphyrin **3**.[3]

(21) Martin, M. L.; Trierweiler, M.; Galasso, V.; Fringuelli, F.; Taticchi, A. *J. Magn. Reson.* **1982**, *47*, 504–506.

The ^{125}Te chemical shift values were nearly identical for **9** and **16−18** (δ 726.7−731.0, Table 1). These values are more similar to the ^{125}Te chemical shift for tellurophene (δ 793)[21] than the ^{125}Te chemical shifts reported for 21-telluraporphyrins **1** (δ 833)[4] and **2** (δ 1039).[4]

^{1}H NMR Spectra. As was reported for the ^{1}H NMR spectrum of **3**,[3] the ditelluraporphyrins **9** and **16−18** undergo conformational changes that are observable on the ^{1}H NMR time scale. The simplest spectra were recorded for ditelluraporphyrin **9**, as shown in Figure 3 (see Supporting Information for ^{1}H NMR spectra of **16−18**.) At +20 °C, the methoxy groups of **9** appeared as two singlets at δ 4.05 and 3.99 integrating for 12 and 24 protons, respectively. At −20 °C, these signals separated into four broadened but distinct signals at δ 4.05, 4.00, 3.98, and 3.95 integrating for 12, 6, 12, and 6 protons, respectively. At +20 °C, two tellurophene protons appeared as a broadened singlet (bandwidth at half-height of >250 Hz) centered at δ 8.6, the four pyrrole protons appeared as a broadened singlet (bandwidth at half-height of ∼55 Hz) centered at δ 7.9, the eight aromatic protons appeared as a broadened singlet centered at δ 7.2 (bandwidth at half-height of ∼55 Hz), and the final two tellurophene protons appeared as a broadened singlet (bandwidth at half-height of >250 Hz) centered at δ 6.2. At −20 °C, the tellurophene protons appeared as two distinct two-proton, broadened singlets (bandwidth at half-height of ∼20 Hz) centered at δ 8.75 and 5.95, the pyrrole protons appeared as two distinct two-proton, broadened singlets (bandwidth at half-height of ∼20 Hz) at δ 8.13 and 7.77, and the eight aromatic protons appeared as a four-proton, broadened singlet (bandwidth at half-height of ∼20 Hz) at δ 7.40 and two two-proton, broadened singlets (bandwidth at half-height of ∼20 Hz) at δ 7.05 and 6.95.

^{13}C NMR Spectra. The ^{13}C NMR spectrum of **9** at −20 °C displayed 18 distinct carbons in the aromatic region (δ 108.7−166.5), including four signals with very similar chemical shifts in the δ 152.0−153.5 region as well as three distinct methoxy carbons (δ 61.3, 61.2, and 56.3, Figure 4). On the basis of the symmetry elements of **9** as shown in structures **3A** and **3B** of Chart 1, one would expect 18 distinct carbon signals in the aromatic region and up to four methoxy signals if rotation of the *meso*-substituents averaged the magnetic environments of the ^{13}C signals in these substituents.

^{1}H−^{13}C COSY experiments at −20 °C (Supporting Information) indicated that the tellurophene protons in the two-proton singlets at δ 8.82 and 5.97 were attached to carbons with ^{13}C chemical shifts δ 142.6 and 159.9, respectively. The two sets of pyrrole protons in the two-proton signals at δ 8.18 and 7.80 were attached to carbons with ^{13}C chemical shifts δ 135.4 and 134.1, respectively. The asymmetry in the tellurophene and pyrrole protons is consistent with having the

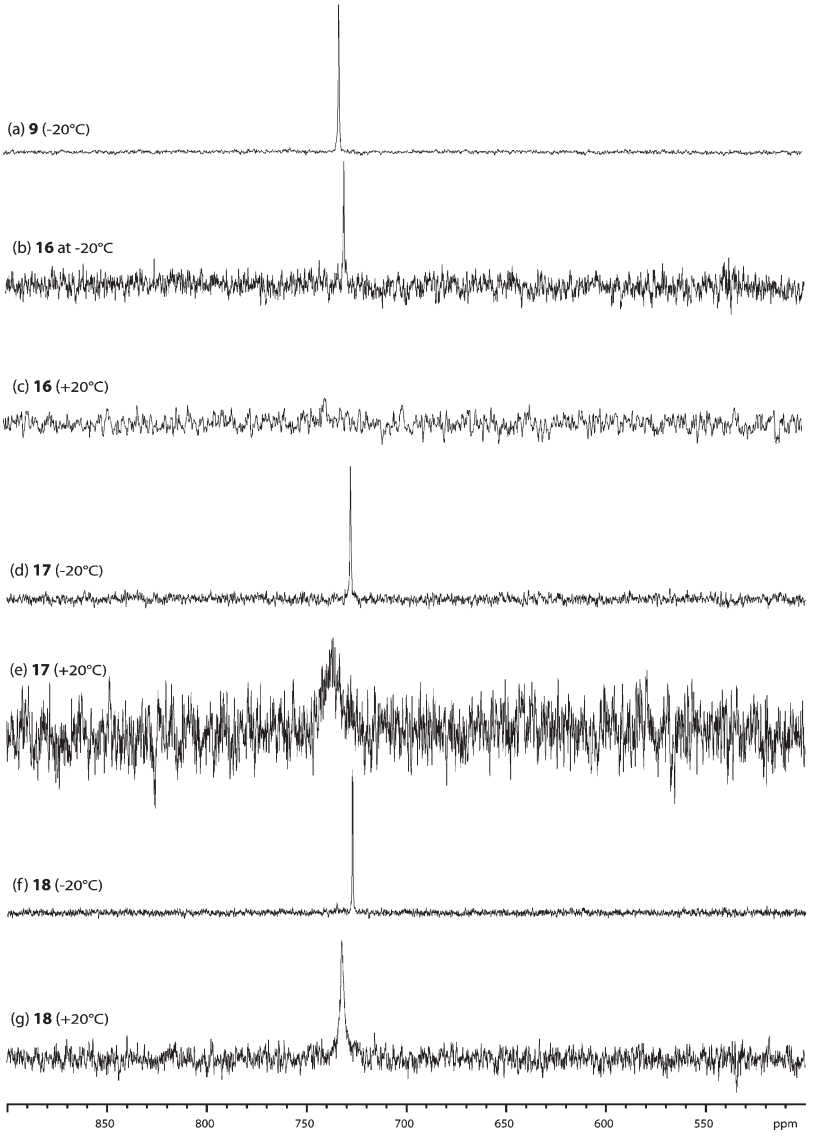


Figure 2. ^{125}Te NMR spectra of 21,23-ditelluraporphyrins **9** at −20 °C and **16**−**18** at −20 and +20 °C.

"normal" and "flipped" tellurophenes in the porphyrin core, as represented by the structure **3A** in Chart 1 with relatively slow interconversion between the two.

In structure **3B** of Chart 1, the two *ortho*-protons on the trimethoxyphenyl substituents would find themselves in different magnetic environments if rotation of the aryl groups were slow. In the ^{1}H NMR spectrum of **9**, the aromatic protons of the trimethoxyphenyl substituents appeared as a four-proton singlet at δ 7.41 and two two-proton singlets at δ 7.10 and 6.95, suggesting that one set of *ortho*-protons sees a single magnetic environment, while the other set of *ortho*-protons sees two different magnetic environments. In ^{1}H−^{13}C COSY experiments, the protons of the four-proton singlet were attached to carbons atoms with a single ^{13}C chemical shift of δ 110.6, while the protons associated with the two-proton singlets at δ 7.10 and 6.95 were also attached to carbon atoms with a single ^{13}C chemical shift of δ 108.7. On the ^{13}C NMR time scale, rotation of the aryl substituents is sufficiently rapid to average the magnetic environments of the individual ^{13}C signals. Consequently, one would expect 18 distinct ^{13}C NMR signals for the telluraporphyrin core, as is observed.

III. Characterization of 26,28-Ditellurasapphyrin 10. X-ray Crystal Structure. Small, thin, green iridescent crystal plates of **10** were grown by vapor diffusion of ethanol into a benzene/dichloromethane solution of **10**. X-ray data from the crystals were refined to give the structure shown in Figure 5. The crystals of **10** contained one benzene and two dichloromethane molecules of crystallization. Tables of crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond lengths and angles for ditellurasapphyrin **10** are compiled in the Supporting Information (Tables 1S−4S, respectively). The 26,28-ditellurasapphyrin core has all five tellurophene and pyrrole rings essentially planar, as shown in Figure 5b. Furthermore, none of the rings are "flipped": all heteroatoms in the rings are pointing toward the interior of the sapphyrin core in the crystal. The Te1···Te2 distance of 3.468 Å, while greater than the sum of covalent radii (2.6 Å), is less than the sum of van der Waals radii for Te (4.12 Å).[21] In the tellurophene rings, Te−C bond lengths were on the order of 2.07−2.08 Å and C−Te−C bond angles were 82.5° and 82.8° at Te1 and Te2, respectively.

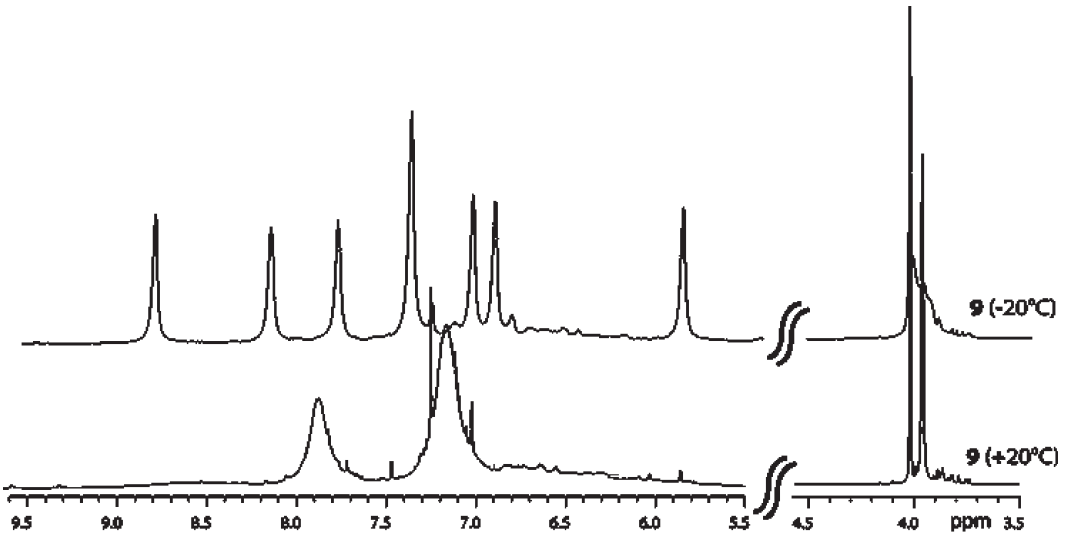


Figure 3. ^{1}H NMR spectra (500 MHz) of 21,23-ditelluraporphyrin **9** in $CDCl_3$ at −20 and +20 °C.

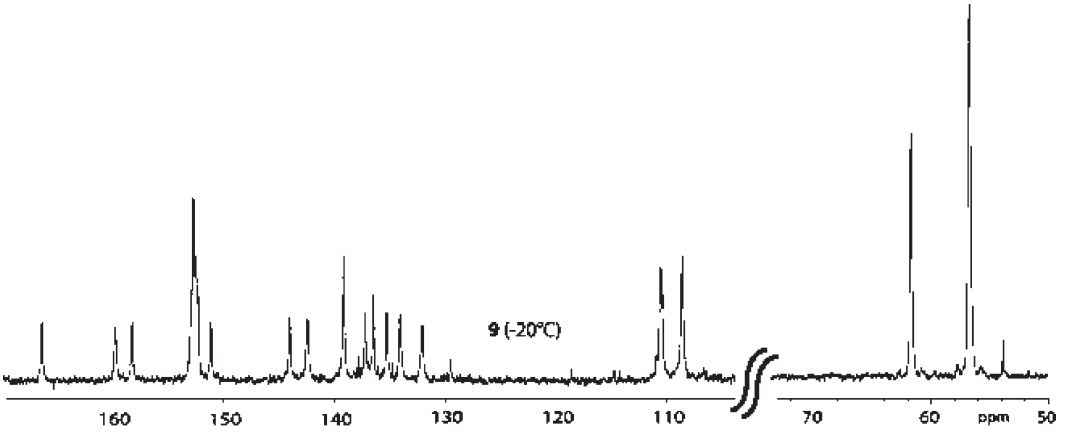


Figure 4. ^{13}C NMR spectrum (125 MHz) of 21,23-ditelluraporphyrin **9** in $CDCl_3$ at −20 °C.

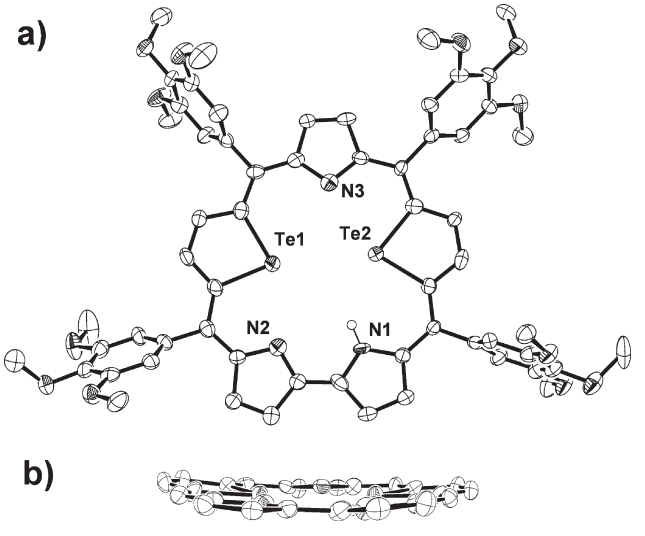


Figure 5. ORTEP drawing with thermal ellipsoids shown at the 50% probability level for the crystal structure of compound **10** viewed (a) from the top and (b) from the side with aryl groups omitted for clarity. With the exception of the tautomeric hydrogen on N1, hydrogen atoms have been omitted for clarity. Solvents of crystallization have also been omitted for clarity.

The X-ray structure shows a tautomer of **10** in which the pyrrole N−H on N1 (position 29) interacts strongly with Te2 but not with Te1. The pyrrole N−H was located from the difference electron density map, and its position was refined and is shown in Figure 5a. The Te···H−N distance is 2.509 Å to the Te2 atom (position 28) and 3.346 Å to the Te1 atom (position 26).

Electronic Spectra. The electronic spectrum of **10** was recorded in $CHCl_3$, and maxima are reported in Table 1. Four major bands ($\varepsilon > 8000\ M^{-1}\ cm^{-1}$) were observed as shown in Figure 1 at 830, 668, 624, and 512 nm. These values are all red-shifted relative to 26,28-diselenasapphyrin **5** (822, 630, 590, and 480 nm, respectively).[10a]

^{125}Te NMR Spectrum. The ^{125}Te NMR spectrum of 26,28-ditellurasapphyrin **10** at −20 °C displayed two signals (δ 731 and 1095, Table 1) separated by 364 ppm (Figure 6). In the X-ray structure of **10**, the two Te atoms are in different chemical and magnetic environments. One Te atom is adjacent to a pyrrole N−H and is capable of accepting a hydrogen bond, while the second Te atom is not. At −20 °C, the 364 ppm difference in chemical shift between the two Te atoms is large, but consistent with two different magnetic and chemical environments for the two Te atoms. The X-ray structure of telluraporphyrin **1** shows Te···H−N

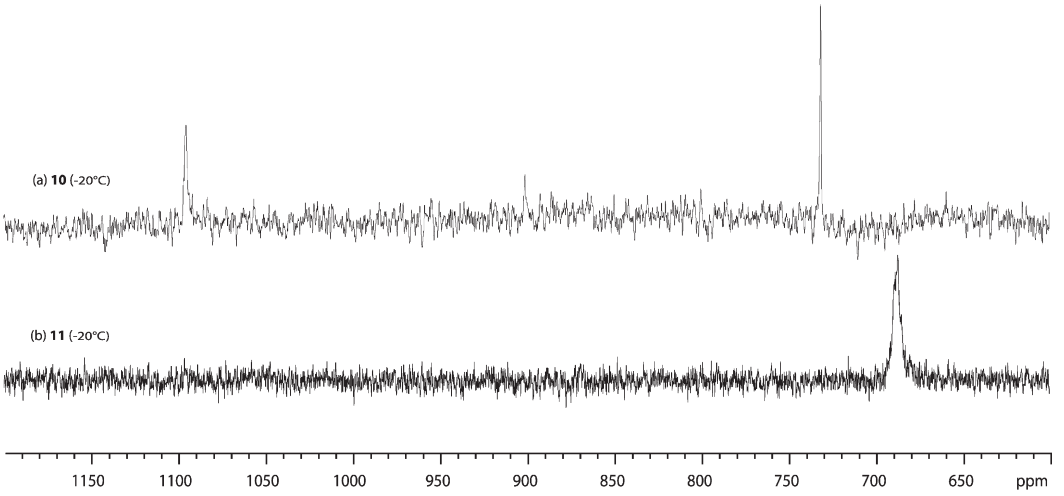


Figure 6. ^{125}Te NMR spectra of (a) 26,28-ditellurasapphyrin **10** and (b) 30,33-ditelluarubyrin **11** at −20 °C.

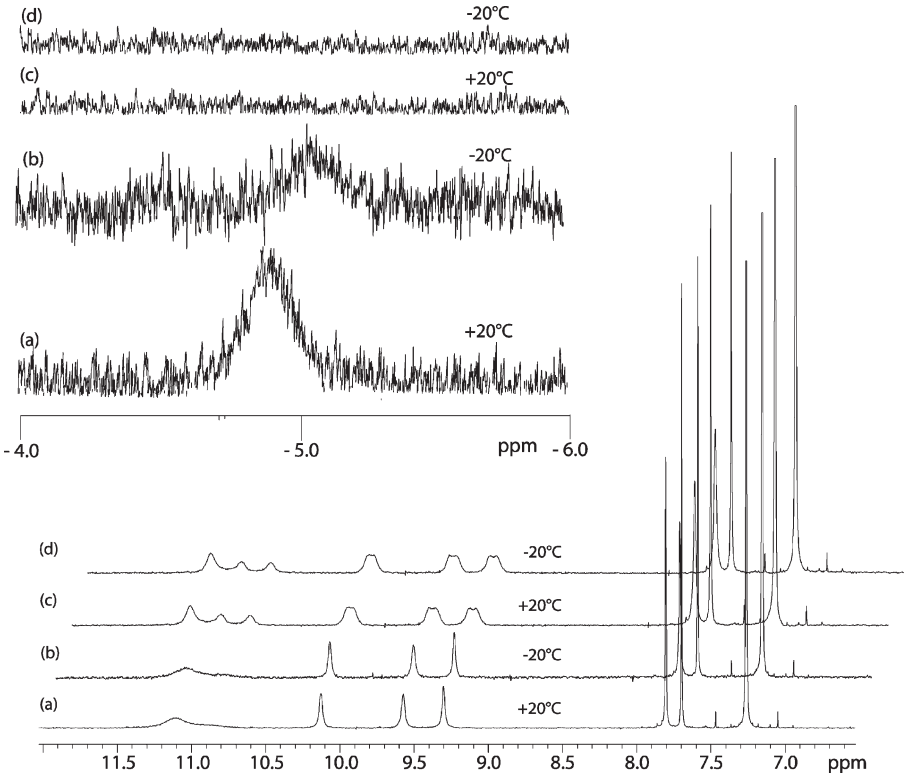


Figure 7. ^{1}H NMR spectra (500 MHz) of the tellurophene/pyrrole/aromatic region (δ 6.5 to 12) and pyrrole N−H region (δ −4 to −6) of 26,28-ditellurasapphyrin **10** in $CDCl_3$ at (a) +20 °C and (b) −20 °C and in $CDCl_3/D_2O$ at (c) +20 °C and (d) −20 °C.

interactions, and the ^{125}Te NMR spectrum of **1** gives a chemical shift of δ 833. In contrast, 21-tellura-23-thiaporphyrin **2** cannot have similar H-bonding interactions, and the ^{125}Te NMR chemical shift observed for the Te atom in the tellurophene ring is δ 1039, a difference of 206 ppm. While the two porphyrin structures are obviously different than the sapphyrin structure, the impact of the pyrrole N−H appears comparable in a comparison of ^{125}Te chemical shifts in the three structures **1**, **2**, and **10**.

^{1}H NMR Spectra. At +20 °C, 26,28-ditellurasapphyrin **10** displays two broadened, two-proton singlets at δ 11.13 (bandwidth at half-height of 50 Hz) and δ 10.90 (bandwidth at half-height >100 Hz) for two different sets of tellurophene protons (Figure 7). The pyrrole protons appear as two two-proton doublets at δ 10.17 and 9.61 (J = 4 Hz) and as a two-proton singlet at δ 9.35. The aromatic protons at the *meso*-positions of **10** appear as two four-proton singlets at δ 7.84 and 7.73 with the downfield signal broadened relative to the upfield signal. The methoxy singlets appear as two six-proton singlets at δ 4.33 and 4.30 and as two 12-proton singlets at δ 4.15 and 4.05. The pyrrolic N−H proton is highly shielded, appearing as a broadened one-proton singlet at δ −4.85 (bandwidth at half-height of ∼60 Hz) and is removed via exchange with D_2O. At −20 °C, the ^{1}H NMR spectrum of **10** was quite similar to the spectrum at +20 °C.

Following D_2O exchange, the rate of tautomerization decreased and eight of the 10 tellurophene/pyrrole protons appeared with unique chemical shifts (Figure 7). Two of the four tellurophene protons appeared as two one-proton

singlets at δ 11.07 (bandwidth at half-height of 35 Hz) and δ 10.87 (bandwidth at half-height of 35 Hz), while the six pyrrole protons appeared as three distinct pairs of protons at δ 10.18 and 10.13, δ 9.65 and 9.58, and δ 9.35 and 9.30 with bandwidths at half-height of ~35 Hz for each signal. The remaining two tellurophene protons appeared as a broadened, two-proton singlet at δ 11.28 (bandwidth at half-height of 40 Hz). The aromatic protons of the 3,4,5-trimethoxyphenyl substituents at the *meso*-positions of **10** appeared as two four-proton singlets at δ 7.84 and 7.73 with the downfield signal broadened relative to the upfield signal. These results suggest that exchange of sites observed in the absence of D_2O is due to N−H tautomerization and not due to ring-flipping as observed with ditelluraporphyrin **3**.[3]

IV. Characterization of 30,33-Ditellurarubyrin 11. Electronic Spectra. The electronic spectrum of 30,33-ditellurarubyrin **11** was recorded in $CHCl_3$, and maxima are reported in Table 1. Five major bands ($\varepsilon \geq 19,000$ M^{-1} cm^{-1}) were observed as shown in Figure 8 at 982, 865, 750, 692, and 641 nm in addition to a strong, Soret-like band at 548 nm (ε 520 000 M^{-1} cm^{-1}). For the most part, these values are red-shifted relative to 5,10,19,24-tetraphenyl-30,33-diselenarubyrin (**7c**) in CH_2Cl_2 (970, 849, 766, 666, and 530 nm).[10a]

^{125}Te NMR Spectra. At −20 °C, 30,33-ditellurarubyrin **11** displays a single ^{125}Te resonance at δ 685 (Figure 6, Table 1). This value is at higher field than the ^{125}Te chemical shifts observed for either 26,28-ditellurasapphyrin **10** or the 21,23-ditelluraporphyrins **9** and **16**−**18**.

^{1}H NMR Spectra. At +20 °C, 30,33-ditellurarubyrin **11** displays two broadened, four-proton singlets at δ 11.18 (bandwidth at half-height of 15 Hz) for the tellurophene protons and δ 10.59 (bandwidth at half-height 15 Hz) for one set of pyrrole protons (Figure 7). The remaining four pyrrole protons appeared as a four-proton doublet (J = 4 Hz) at δ 9.75. The aryl protons of the 3,4,5-trimethoxyphenyl substituents appeared as an eight-proton singlet at δ 7.95, and the methoxy signals appeared as a 12-proton singlet at δ 4.34 and as a 24-proton singlet at δ 4.13. The two pyrrolic N−H protons were apparent as a broad singlet at δ −5.60 (bandwidth at half-height of 800 Hz) and were removed by exchange with D_2O. At −20 °C, the ^{1}H NMR spectrum of **11** was relatively unchanged relative to that at +20 °C.

Following exchange with D_2O, tautomerization of the N−D deuterons is slower than tautomerization of the pyrrolic N−H protons prior to exchange. Consequently, the signals for the tellurophene protons at δ 11.18 and the pyrrole protons at δ 10.59 and 9.75 are broadened relative to those prior to D_2O exchange. At −20 °C, the broadening is more extensive.

^{13}C NMR Spectra. The ^{13}C NMR spectrum of **11** was acquired at −20 °C with discrete signals observed at δ 152.5, 137.8, 112.2, 62.0, and 56.9 (Figure 10) corresponding to five of the six signals expected for the 3,4,5-trimethoxyphenyl substituents (four different aromatic carbons, two different methoxy carbons). The remaining ^{13}C signals were contained in two broadened signals (bandwidth at half-height of 25 Hz) centered at δ 141 and 133. Following D_2O exchange, the signals at δ 152.5, 137.8, 112.2, 62.0, and 56.9 were unchanged, but the broadened signals at δ 141 and 133 started to resolve into several signals.

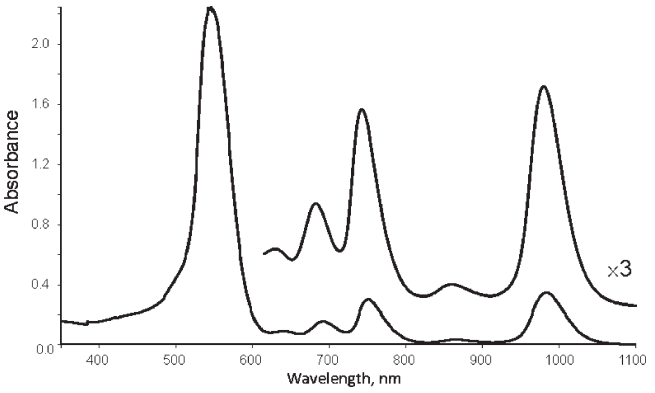


Figure 8. Electronic spectrum of 30,33-ditellurarubyrin **11** (3.8×10^{-6} M) in $CHCl_3$.

Summary and Conclusions

We have developed a synthetic approach to 2,5-di(arylhydroxymethyl)tellurophenes **12** utilizing the addition of Li_2Te to diyndiols **13**. The Li_2Te was generated by the reduction of Te powder with lithium triethylborohydride. No additional Lewis acid was necessary. The method tolerated not only phenyl substituents but also 4-methoxphenyl and 3,4,5-trimethoxyphenyl substituents. The 2,5-di(arylhydroxymethyl)tellurophenes **12**

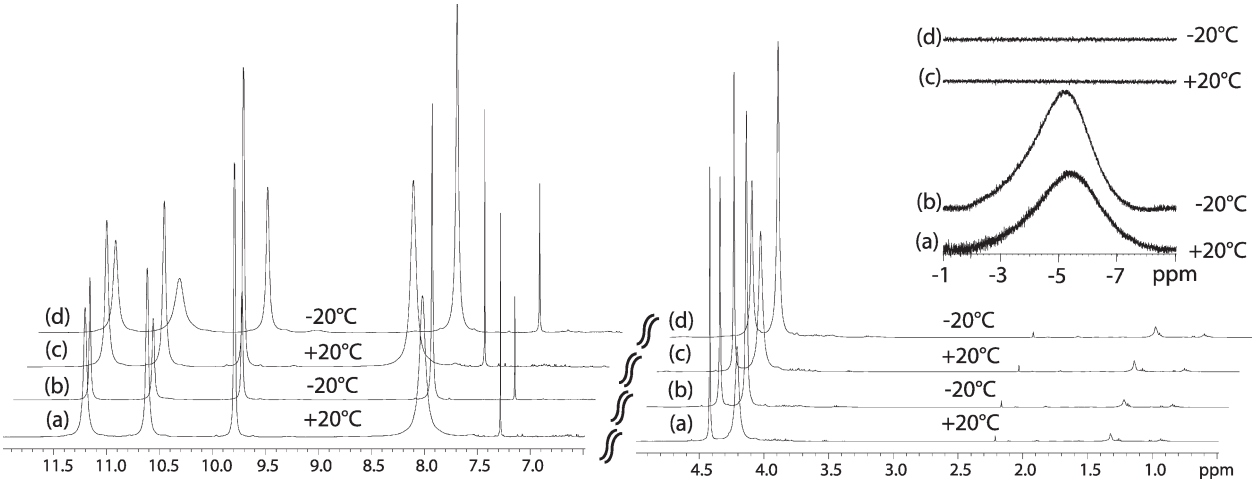


Figure 9. ^{1}H NMR spectra (500 MHz) of 30,33-ditellurarubyrin **11** in $CDCl_3$ at (a) +20 °C and (b) −20 °C and in $CDCl_3/D_2O$ at (c) +20 °C and (d) −20 °C.

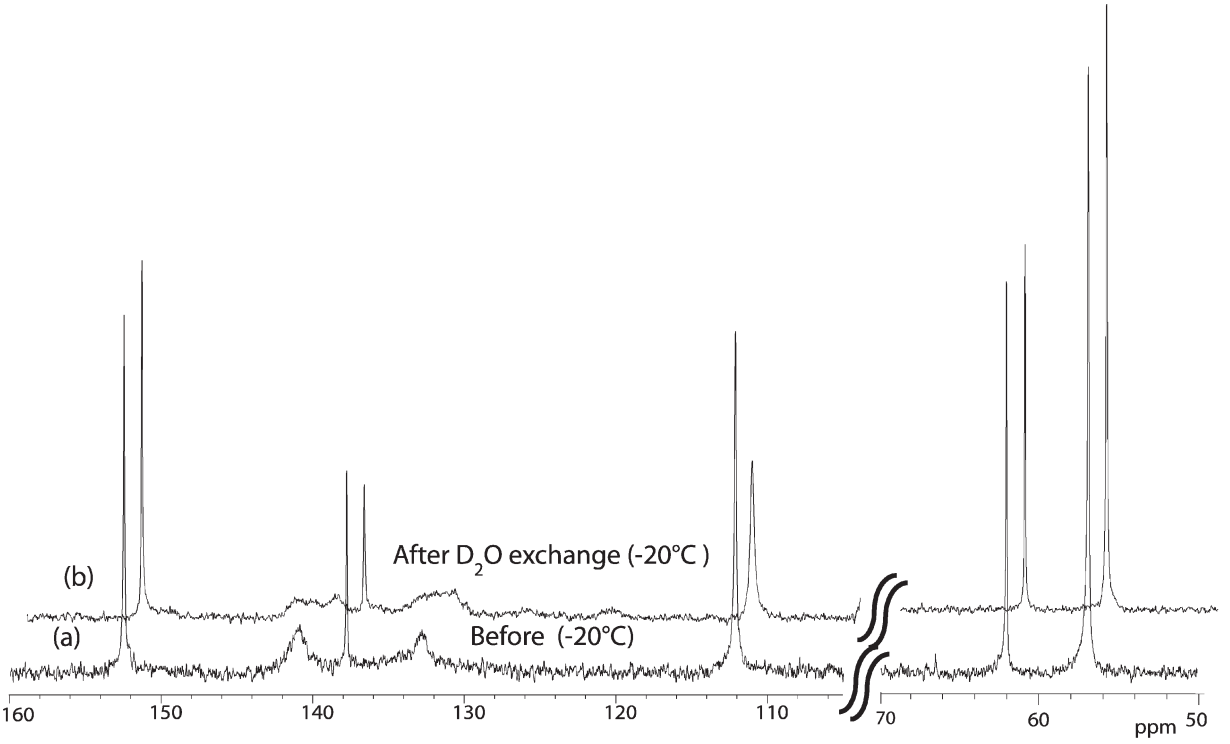
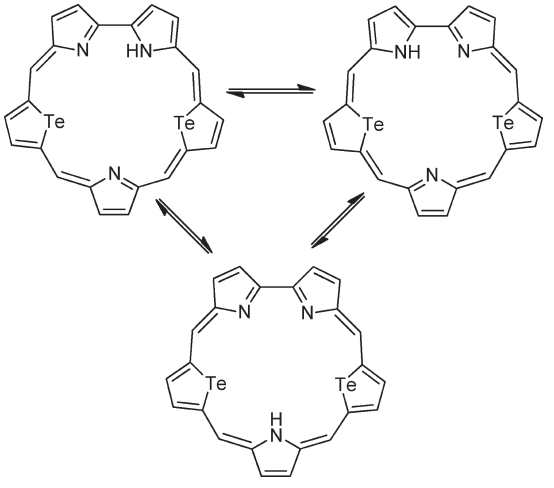


Figure 10. ^{13}C NMR spectrum (125 MHz) of 30,33-ditellurarubyrin **11** at −20 °C (a) in $CDCl_3$ and (b) in $CDCl_3/D_2O$.

Scheme 3



were converted to ditelluraporphyrins **3**, **9**, and **16**−**18** by reaction of **12** with the appropriate dipyrranotellurophenes **15** and BF_3−etherate in CH_2Cl_2 followed by oxidation of the initial product with *p*-chloranil (Scheme 2).

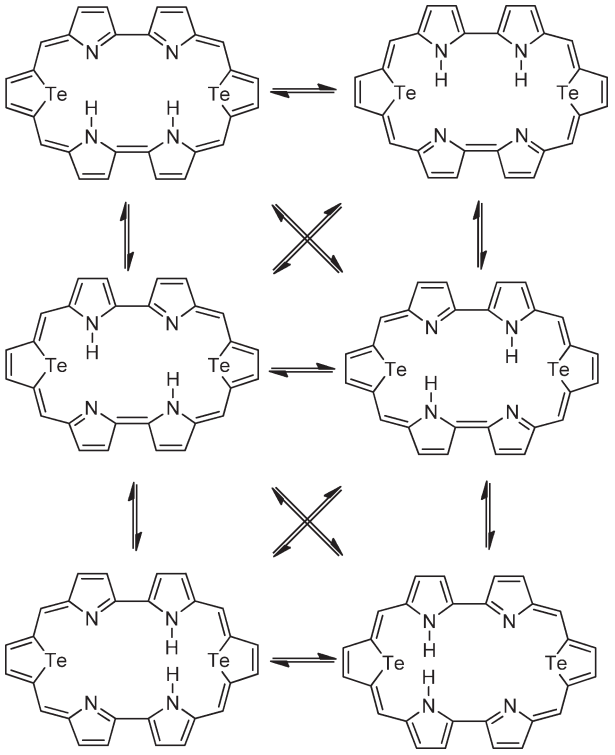
The novel 21,23-ditelluraporphyrins **9** and **16**−**18** displayed the same dynamic processes as had been previously observed with **3** in the temperature-dependent ^1H NMR spectra of these compounds.[3] The ^{125}Te NMR spectra of **9** and **16**−**18** displayed a single peak at −20 °C, suggesting that the interconversion of "normal" and "flipped" tellurophenes as shown in Chart 1 was sufficiently rapid at this temperature to give an averaged signal.

A minor product isolated from the synthesis of **9** was 26,28-ditellurasapphyrin **10**, which is a novel heterocyclic structure. The X-ray structure of **10** has all five tellurophene and pyrrole rings essentially planar with all heteroatoms in the rings pointing toward the interior of the sapphyrin core. The ditellurasapphyrin **10** displayed two distinct signals in the ^{125}Te NMR spectrum separated by ∼350 ppm, perhaps reflecting the effects of H-bonding from a pyrrole NH (N1 in Figure 3) to one Te atom (Te2 in Figure 3). In spite of the influence of the pyrrole N−H, the two tellurophene rings have comparable Te−C bond lengths of 2.07−2.08 Å and comparable C−Te−C bond angles of 82.5° and 82.8°, which are "normal" values for tellurophene rings (Table 4S in Supporting Information).[22] The ditellurasapphyrin **10** also displayed dynamic processes in the ^1H and ^{13}C NMR spectra of the compound, but the rate of these processes slowed following D_2O exchange of the pyrrole NH, suggesting that the interconversion of pyrrole tautomers is responsible for the dynamic processes as shown in Scheme 3 (with the 3,4,5-trimethoxyphenyl groups omitted for clarity).

30,33-Ditellurarubyrin **11** was synthesized independently from the reaction of dipyrrane **15c** with 2 equiv of trifluoroacetic acid followed by oxidation with *p*-chloranil.[10a] The ditellurarubyrin **11** displayed one signal in its ^{125}Te NMR spectrum at 685 ppm. The ditellurarubyrin **11** also displayed dynamic processes in the ^1H and ^{13}C NMR spectra of the compound, but the rate of these processes slowed following D_2O exchange of the pyrrole NH, suggesting that the interconversion of pyrrole tautomers is responsible for the dynamic processes as shown in Scheme 4 (with the 3,4,5-trimethoxyphenyl groups omitted for clarity). The bandwidth at half-height of the pyrrole NH in **11** is > 500 Hz (Figure 9), which is consistent with exchange at multiple sites.

(22) (a) Fanfani, L.; Nunzi, A.; Zanazzi, P. F.; Zanzari, A. R.; Pellinghelli, M. A. *Cryst. Struct. Commun.* **1972**, *1*, 273–278. (b) Zukerman-Schpector, J.; Daboub, M. J.; Dadboub, V. B.; Pereira, M. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *C48*, 767–768. (c) Catalano, D.; Caporusso, A. M.; Da Settimo, F.; Forte, C.; Veracini, C. A. *Gazz. Chim. Ital.* **1988**, *118*, 529–532.

Scheme 4



The photophysical properties (quantum yields for triplet formation and singlet oxygen generation, rates of internal conversion and intersystem crossing, radiative lifetimes) of these new Te-containing heterocyclic systems have yet to be explored. The methoxy substituents provide a handle for the preparation of water-soluble analogues that may have potential as photosensitizers[13] and membrane probes.[14]

Experimental Section

5,10,15,20-Tetraphenyl-21,23-ditelluraporphyrin (3).[3] Borontrifluoride−etherate (0.290 g, 2.04 mmol) was added to dipyrrolotellurophene **15a** (2.00 g, 4.08 mmol) and tellurophene **12a** (1.46 g, 4.08 mmol) in 1200 mL of degassed CH_2Cl_2, and the reaction mixture was stirred for 1 h in the dark at ambient temperature. *p*-Chloranil (4.01 g, 16.3 mmol) was added, and the resulting mixture was heated at reflux for 1 h in the dark. The reaction mixture was concentrated, and the product was purified on basic Al_2O_3 (CH_2Cl_2). The first green band was collected, concentrated, and recrystallized (acetone/MeOH) to give 1.17 g (34%) of **3** as a dark green solid, mp > 300 °C.

5,10,15,20-Tetra(3,4,5-trimethoxyphenyl)-21,23-ditelluraporphyrin (9). Dipyrrolotellurophene **15c** (0.40 g, 0.60 mmol) and **12c** (0.34 g, 0.60 mmol) in 180 mL of degassed CH_2Cl_2, BF_3−etherate (0.043 g, 0.30 mmol), and *p*-chloranil (0.59 g, 2.4 mmol) were treated as described for the preparation of **3**. The first green band was collected, concentrated, and recrystallized twice from 5:95 EtOH/$CHCl_3$ to give 0.089 g (12%) of **9** as dark green crystals, mp > 300 °C: ^{1}H NMR (500 MHz, $CDCl_3$, 253 K) δ 8.82 (s, 2 H), 8.18 (s, 2H), 7.80 (s, 2 H), 7.41 (s, 4 H), 7.10 (s, 2 H), 6.95 (s, 2 H), 5.97 (s, 2 H), 4.06 (s, 24 H), 4.01 (s, 6 H), 3.97 (s, 6 H); ^{13}C NMR (125.7 MHz, $CDCl_3$, 253 K) δ 166.5, 159.9, 158.4, 152.9, 152.6, 151.3, 144.2, 142.6, 139.3, 137.2, 136.8, 135.4, 134.1, 132.6, 129.7, 114.9, 110.6, 108.7, 61.3, 61.2, 56.3; HRMS (ES) *m*/*z* 1205.1702 (calcd for $C_{56}H_{52}N_2O_{12}{}^{130}Te_2 + H^+$: 1205.1717). Anal. Calcd for $C_{56}H_{52}N_2O_{12}Te_2$: C, 56.04; H, 4.37; N, 2.33. Found: C, 56.29; H, 4.23; N, 2.33.

5,10,15,20-Tetra(3,4,5-trimethoxyphenyl)-26,28-ditellurasapphyrin (10). Preceding the first green band in the chromatographic separation of **10** from the reaction of **7c** and **4c** described above was a reddish pink band, which was collected and concentrated. The crystalline residue was recrystallized from $CHCl_3$/EtOH to give 0.008 g (0.6%) of ditellurasapphyrin **10** as dark purple crystals, mp > 300 °C: ^{1}H NMR (500 MHz, $CDCl_3$, 253 K) δ 11.18 (br s, 2 H), 11.02 (br s, 2 H), 10.22 (br s, 2 H), 9.66 (br s, 2 H), 9.39 (br s, 2 H), 7.87 (br s, 4 H), 7.75 (s, 4 H), 4.34 (s, 3 H), 4.31 (s, 3 H), 4.14 (s, 6 H), 4.06 (br s, 6 H), −5.02 (br s, 1 H); ^{1}H NMR (500 MHz, $CDCl_3/D_2O$, 253 K) δ 11.30 (br s, 2 H), 11.10 (br s, 1 H), 10.88 (br s, 1 H), 7.87 (br s, 4 H), 7.75 (s, 4 H), 4.34 (s, 3 H), 4.31 (s, 3 H), 4.14 (s, 6 H), 4.06 (br s, 6 H). Anal. Calcd for $C_{60}H_{55}N_3O_{12}Te_2 \cdot CHCl_3$: C, 52.91; H, 4.08; N, 3.03. Found: C, 53.08; H, 4.11; N, 2.97.

5,10,19,24-Tetra(3,4,5-trimethoxyphenyl)-30,33-ditellurarubyrin (11). Trifluoroacetic acid (0.088 mL, 1.2 mmol) was added to a stirred solution of dipyrrolotellurophene **15c** (0.40 g, 0.60 mmol) in 300 mL of dry, degassed CH_2Cl_2 in a foil-covered flask. After 2 h, *p*-chloranil (0.44 g, 1.8 mmol) was added and the resulting solution was heated at reflux for 1 h. The reaction mixture was neutralized with Et_3N and concentrated. The residue was purified via chromatography on Al_2O_3 eluted with $CHCl_3$. The first band was collected and recrystallized from acetone to give 0.13 g (32%) of **11** as shiny green crystals, mp > 300 °C (dec): ^{1}H NMR (500 MHz, $CDCl_3$, 253 K) δ 11.31 (s, 4 H), 10.71 (s, 4 H), 9.88 (d, 4 H, II = 4 Hz), 8.07 (s, 8 H), 4.42 (12 H), 4.21 (s, 24 H), −5.5 (br s, 2 H); ^{13}C NMR (125.7 MHz, $CDCl_3$, 253 K) δ 152.5, 141 (br), 137.9, 133 (br) 112.2, 62.0, 55.9; MS (ES) *m*/*z* 1335 ($C_{64}H_{58}N_4O_{12}{}^{130}Te_2 + H^+$: 1335). Anal. Calcd for $C_{64}H_{58}N_4O_{12}Te_2$: C, 57.78; H, 4.39; N, 4.21. Found: C, 57.81; H, 4.44; N, 4.18.

2,5-Di(1-hydroxy-1-phenylmethyl)tellurophene (12a). [2] Lithium triethylborohydride (1.0 M in THF, 18.3 mL, 18.3 mmol) was added to Te powder (1.17 g, 9.15 mmol) under argon, and the resulting mixture was stirred for 0.5 h at ambient temperature. Diyndiol **13a** (2.0 g, 7.6 mmol) in 80 mL of degassed EtOH was added. The resulting mixture was stirred for 4 h. Saturated NH_4Cl (100 mL) was added, and products were extracted with CH_2Cl_2 (3 × 75 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered through Celite, and concentrated. The crude product was precipitated and recrystallized from a 1:1 solution of CH_2Cl_2/hexanes to give 1.3 g (44%) of **13a** as a white solid, mp 145−146 °C: ^{1}H NMR (CD_3OD_3, 500 MHz) δ 7.40 (d, 4 H, *J* = 8 Hz), 7.29 (t, 4 H, *J* = 8 Hz), 7.23 (t, 2 H, *J* = 8 Hz), 7.21 (s, 2 H), 5.70 (s, 2 H); ^{13}C NMR (CD_3OD, 75 MHz) δ 158.4, 146.7, 133.3, 129.3, 128.5, 127.3, 77.5; HRMS (EI) *m*/*z* 376.0105 (calcd for $C_{18}H_{16}O_2{}^{130}Te^+ - H_2O$: 376.0101). Anal. Calcd for $C_{18}H_{16}O_2Te$: C, 55.16; H, 4.11. Found: C, 55.22; H, 4.09.

2,5-Di[hydroxy(4-methoxyphenyl)methyl]tellurophene (12b). Lithium triethylborohydride (1.0 M in THF, 14.5 mL, 14.5 mmol), Te powder (0.95 g, 7.5 mmol), and diyndiol **13b** (2.0 g, 6.2 mmol) in 100 mL of EtOH were treated as described for the synthesis of **12a** to give 2.0 g (71%) of **12b** as a white solid, as a 1:1 mixture of diastereomers by ^{1}H NMR, mp 121−124 °C: Distinct pairs of diastereomeric protons and carbons are indicated by * (spectra in Supporting Information); ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 (AA′BB′, 4 H, *J* = 8 Hz, *), 7.30 (AA′BB′, 4 H, *J* = 8 Hz, *), 7.18 (s, 2 H, *), 7.17 (s, 2 H, *), 6.85 (AA′BB′, 4 H, *J* = 8 Hz), 5.66 (s, 2 H), 3.77 (s, 6 H, *), 3.76 (s, 6 H, *); ^{13}C NMR (75 MHz, CD_3OD) δ 160.6, 158.5 (*), 158.4 (*), 138.81 (*), 138.78 (*), 133.2, 128.61 (*), 128.59 (*) 114.7, 77.1, 55.7; HRMS (ES) *m*/*z* 477.0331 (calcd For $C_{20}H_{20}O_4{}^{130}Te + Na^+$: 477.0332). Anal. Calcd for $C_{20}H_{20}O_4Te$: C, 53.15; H, 4.46. Found: C, 53.27; H, 4.48.

2,5-Di[hydroxy(3,4,5-trimethoxyphenyl)methyl]tellurophene (12c). Lithium triethylborohydride (1.0 M in THF, 14.5 mL, 14.5 mmol), Te powder (0.95 g, 7.5 mmol), and diyndiol **13c** (2.7 g, 6.2 mmol) in 100 mL of degassed EtOH were treated as described for the synthesis of **12a** to give 3.7 g (71%) of **12c** as a white solid, as a 1:1 mixture of diastereomers by ^{1}H NMR, mp 194−195 °C: Distinct pairs of diastereomeric protons and carbons are indicated by * (spectra in Supporting Information); ^{1}H NMR (400 MHz, CD_3OD) δ 7.27 (s, 2 H, *), 7.26 (s, 2 H, *), 6.74 (s, 4 H, *), 6.73 (s,

4 H, *), 5.66 (s, 2 H, *), 5.65 (s, 2 H, *), 3.81 (s, 12 H, *), 3.79 (s, 12 H, *), 3.73 (s, 6 H, *), 3.72 (s, 6 H, *); ^{13}C NMR (75 MHz, acetone-d_6) δ 158.3 (*), 158.1 (*), 154.3, 142.3, 138.4, 132.4, 104.4, 76.8, 60.44 (*), 60.42 (*), 56.39 (*), 56.38 (*); HRMS (ES) m/z 597.0748 (calcd for $C_{24}H_{26}O_8{}^{130}Te + Na^+$: 597.0739). Anal. Calcd for $C_{24}H_{26}O_8Te$: C, 50.39; H, 4.93. Found: C, 50.47; H, 4.88.

2,5-Di[2-pyrrolo(phenyl)methyl]tellurophene (15a). Borontrifluoride−etherate (0.34 g, 2.4 mmol) was added to tellurophene **12a** (1.90 g, 4.85 mmol) in degassed pyrrole (60 mL), and the resulting mixture was stirred for 1 h under argon. The reaction was diluted with CH_2Cl_2, and 40% NaOH (25 mL) was added. The organic layer was separated, washed with water (3 × 100 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated. Excess pyrrole was removed via distillation at 50 °C (20 Torr), and the product was purified on SiO_2 (70:30 hexanes/EtOAc) to give 2.24 g (94%) of **15a** as a brown oil that was used without further purification: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (s, 2 H), 7.25 (s, 2 H), 7.25−6.81 (m, 10 H), 6.66 (s, 2 H), 6.12 (s, 2 H), 5.97 (s, 2 H), 5.47 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5, 144.4, 134.7, 134.4, 128.6, 128.2, 127.0, 117.7, 117.2, 108.2, 107.1; HRMS (EI) m/z 492.0847 (calcd for $C_{26}H_{22}N_2Te^+$: 492.0840).

2,5-Di[2-pyrrolo(4-methoxyphenyl)methyl]tellurophene (15b). Tellurophene **12b** (1.50 g, 3.32 mmol), pyrrole (15 mL), and BF_3 etherate (0.22 g, 1.6 mmol) were treated as described for **15a** to give 1.59 g (87%) of **15b** as a brown oil that was used without further purification: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (br s, 2 H), 7.24 (s, 2 H), 7.19 (d, 4 H, J = 7 Hz), 6.82 (d, 4 H, J = 7 Hz), 6.67 (s, 2 H), 6.12 (s, 2 H), 5.97 (s, 2 H), 5.43 (s, 2 H), 3.78 (s, 6 H); HRMS (ES) m/z 553.1124 (calcd for $C_{28}H_{26}N_2O_2{}^{130}Te + H^+$: 553.1129).

2,5-Di[2-pyrrolo(3,4,5-trimethoxyphenyl)methyl]tellurophene (15c). Tellurophene **12c** (3.00 g, 5.42 mmol), pyrrole (30 mL), and BF_3−etherate (0.22 g, 1.6 mmol) were treated as described for **15a** to give 3.49 g (99%) of **15c** as a brown oil that was used without further purification: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (br s, 2 H), 7.30 (s, 2 H, J = 4.5 Hz), 6.69 (s, 2 H), 6.51 (s, 4 H), 6.15 (s, 2 H), 6.01 (s, 2 H), 5.40 (s, 2 H), 3.83 (s, 6 H), 3.78 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 153.3, 140.2, 137.1, 134.2, 134.3, 117.3, 108.4, 107.3, 105.5, 60.9, 56.2, 51.4; HRMS (ES) m/z 695.1363 (calcd for $C_{32}H_{34}N_2O_6{}^{130}Te + Na^+$: 695.1371).

5,20-Di(4-methoxyphenyl)-10,15-diphenyl-21,23-ditelluraporphyrin (16). Dipyrrolotellurophene **15a** (2.00 g, 4.08 mmol) and tellurophene **12b** (1.84 g, 4.08 mmol) in 1800 mL of degassed CH_2Cl_2, BF_3−etherate (0.290 g, 2.04 mmol), and *p*-chloranil (4.01 g, 16.3 mmol) were treated as described for **3**. The first green band was collected, concentrated, and recrystallized using acetone/MeOH to give 1.01 g (28%) of **16** as a green solid, mp > 300 °C: ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) δ 8.28 (br s, 2 H), 8.08 (br d, J = 8.5 Hz) and 7.92 and 7.75 (br d, J = 4 Hz) [4 *o*-protons of the 4-methoxyphenyl and 4 *o*-protons of the phenyl substituents, 8 H total], 7.87 (br s, 2 H), 7.78 (br s, 2 H), 7.59 (t, 4 H, J = 7 Hz), 7.53 (t, 2 H, J = 7 Hz), 7.13 (d, 4 H, J = 8.5 Hz), 6.41 (br s, 2 H), 3.96 (s, 4 H); HRMS (ES) m/z 921.0616 (calcd for $C_{46}H_{32}N_2O_2{}^{130}Te_2 + HO^+$: 921.0626). Anal. Calcd for $C_{46}H_{32}N_2O_2Te_2$: C, 61.39; H, 3.58; N, 3.11. Found: C, 61.62; H, 3.91; N, 3.42.

5,10,15,20-Tetra(4-methoxyphenyl)-21,23-ditelluraporphyrin (17). Dipyrrolotellurophene **15b** (1.50 g, 2.73 mmol) and **12b** (1.23 g, 2.73 mmol) in 1500 mL of degassed CH_2Cl_2, BF_3−etherate (0.19 g, 1.4 mmol), and *p*-chloranil (2.68 g, 10.9 mmol) were treated as described for the preparation of **3**. The first green band was collected, concentrated, and recrystallized using acetone/MeOH to give 0.50 g (19%) of **17** as dark green crystals, mp > 300 °C: ^{1}H NMR (500 MHz, $CDCl_3$, 253 K) δ 8.50 (br s, 2 H), 8.10 (br s, 2 H), 7.98 (br s, 2H), 7.68 (br s, 2 H), 7.60 (br s, 2 H), 7.14 (d, 4 H), 6.21 (br s, 2 H), 3.98 (s, 12 H); HRMS (EI) m/z 964.0891 (calcd for $C_{48}H_{36}N_2O_2{}^{130}Te_2{}^+$: 964.0800). Anal. Calcd for $C_{48}H_{36}N_2O_2Te_2$: C, 60.05; H, 3.78; N, 2.92. Found: C, 60.12; H, 3.73; N, 2.89.

5,20-Bis(3,4,5-trimethoxyphenyl)-10,15-di(4-methoxyphenyl)-21,23-ditelluraporphyrin (18). Dipyrrolotellurophene **15c** (1.78 g, 2.66 mmol) and **12b** (1.20 g, 2.66 mmol) in 1600 mL of degassed CH_2Cl_2, BF_3 etherate (0.114 g, 0.80 mmol), and *p*-chloranil (2.61 g, 10.6 mmol) were treated as described for the preparation of **3**. The last green band was repurified via chromatography on basic Al_2O_3 (30:70 EtOAc/hexanes) to give 0.34 g (13%) of **19** as dark green crystals, mp > 300 °C, following recrystallization from acetone/MeOH. ^{1}H NMR (500 MHz, $CDCl_3$, 253 K) δ 8.56 (s, 2 H), 8.13 (br d, 4 H), 8.00 (s, 2 H), 7.62 (s, 2 H), 7.15 (d, 4 H, J = 8.5 Hz), 6.99 (s, 2 H), 6.89 (s, 2 H), 6.29 (s, 2 H), 4.05 (s, 6 H), 3.965 (br s, 12 H), 3.945 (br s, 6 H); HRMS (ES) m/z 1101.1279 (calcd. for $C_{52}H_{44}N_2O_8{}^{130}Te_2 + HO^+$: 1101.1250). Anal. Calcd for $C_{52}H_{44}N_2O_8Te_2$: C, 57.82; H, 4.11; N, 2.59. Found: C, 58.01; H, 4.13; N, 2.73.

X-ray Diffraction Data. X-ray diffraction data on **10** were collected at 90(1) K using a Bruker SMART APEX2 CCD diffractometer installed at a rotating anode source (Mo Kα radiation, λ = 0.71073 Å) and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with a 0.5° frame-width (ω scan) and 60 s exposure time per frame. Four sets of data (360 frames in each set) were collected for each compound, nominally covering complete reciprocal space. The data were integrated, scaled, sorted, and averaged using the APEX2 software package.[22] The structure was solved by direct methods using SHELXTL version 2008/4.[23] The structure was refined by full-matrix least-squares against F^2.

Non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were found by difference electron density Fourier synthesis. The CH_3 hydrogens were treated as part of idealized CH_3 groups with $U_{iso} = 1.5U_{eq}$, while the remainder of the hydrogen atoms were refined with the "riding" model with $U_{iso} = 1.2U_{eq}$.

Crystallographic data are compiled in Table 1S in the Supporting Information. Atomic coordinates, anisotropic displacement parameters, and bond lengths and angles are given in Tables 2S−4S, respectively, in the Supporting Information.

NMR Spectral Data. The NMR samples were prepared in $CDCl_3$ in 5 mm NMR tubes. The ^{125}Te NMR spectra were recorded on a Varian Inova-400 NMR spectrometer at 126.289 MHz and 55 °C. The spectral width for acquisition was set to 320 kHz with an acquisition time of 0.82 s. The data were collected for 16K transients, with a pulse width of 9 μs and a relaxation delay of 3−4 s. The FIDs were transformed with an exponential line broadening function of 10−15 Hz. 1D ^{1}H, ^{2}H, and ^{13}C data and 2D ^{1}H, ^{13}C-HSQC data were acquired on a Varian Inova-500 NMR spectrometer using standard Varian pulse sequences and parameters.

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Supporting Information Available: General experimental details, synthetic procedures for the preparation of **13a−c** and **14a−c**, tables of crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond lengths and angles for **10**, ^{1}H NMR spectra for **16−18**, partial ^{1}H−^{13}C COSY spectrum for **9**, HRMS data for **9** and **16−18**, and ^{1}H and ^{13}C NMR spectra for tellurophenes **12b** and **12c**. This material is available free of charge via the Internet at http://pubs.acs.org.

(23) *APEX2*, Area Detector Control and Integration Software, Ver. 2008.4-0; Brüker Analytical X-ray Systems: Madison, WI. 2008.

(24) *SHELXTL*, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Ver. 2008/4; Brüker Analytical X-ray Systems: Madison, WI, 2008.