Thiol-Derivatized Porphyrins for Attachment to Electroactive Surfaces

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The attachment of porphyrin monomers and multiporphyrin arrays in controlled architectures on electroactive surfaces opens many opportunities for electrochemical studies. Toward this goal, we have developed routes for the preparation of thiol-derivatized porphyrin monomers and porphyrin building blocks that require minimal or no handling of free thiols. Routes to *S*-protected *p*-thiobenzaldehydes and *m*-(thiomethyl)benzaldehydes have been developed. Two sets of meso-substituted porphyrins with variation in electrochemical potentials have been prepared for vertical or horizontal orientation with respect to the electroactive surface. In one set, each porphyrin bears one *S*-protected *p*-thiophenyl unit and substituents at the three remaining *meso*-positions. In the other set each porphyrin possesses four *S*-protected *m*-(thiomethyl)phenyl units. Tuning the electrochemical potential in the former set has been achieved by variation of the meso substituents (mesityl, 2,4,6-trimethoxyphenyl, *n*-pentyl, pentafluorophenyl) and in the latter set by variation of the central metal (Zn, Cu, Co, Ag). Six thiol protecting groups [*S*-cyano, *S*-(*N*-ethylcarbamoyl), *S*-acetyl, *S*-(9-anthrylmethyl), *S*-(2,4-dinitrophenyl), *S*-pivaloyl] have been found to be compatible with porphyrin formation and metalation with zinc. The *S*-cyano, *S*-(*N*-ethylcarbamoyl), and *S*-acetyl groups undergo in situ cleavage and/or binding on a gold surface. Of these three, only the *S*-acetyl protecting group is compatible with the Pd-mediated iodo-ethyne coupling conditions for the preparation of multiporphyrin arrays. Three trans-substituted porphyrin building blocks have been prepared for the synthesis of multiporphyrin arrays that can be attached to an electroactive surface. One porphyrin has two mesityl, one *p*-iodophenyl, and one *p*-(*S*-acetylthio)phenyl substituent for vertical positioning, and two porphyrins each have two *m*-iodophenyl and two *S*-protected *m*-(thiomethyl)phenyl substituents for horizontal positioning. Altogether, 16 free base and 16 metalloporphyrins have been prepared. This work establishes the foundation for preparing diverse thiol-derivatized porphyrin monomers and building blocks.

Introduction

As part of a program in molecular electronics, we sought to attach porphyrin-based molecular devices to an electroactive surface. The molecular devices of interest range from simple monomeric porphyrins to multiporphyrin arrays such as optoelectronic gates[1] and integrated antenna-reaction center complexes.[2] We sought to be able to (1) attach monomeric porphyrins of varying redox potentials in a vertical or horizontal arrangement on the gold surface, (2) make attachments to specific porphyrins in a multiporphyrin array, and (3) employ linkers that afford facile electronic communication between the porphyrin and the electroactive surface. A common approach for attaching organic molecules to an electroactive surface such as gold involves the use of thiol substituents. Indeed, the use of thiophenol linkers has enabled rapid electron-transfer reactions between redox-active substituents and a gold electrode.[3]

A large number of porphyrin monomers bearing thiols have been prepared,[4−14] and some have been attached to gold electrodes.[15,16] The prevalent synthetic route to porphyrin thiols involves the derivatization of a substituted porphyrin with a thiol reagent or protected thiol unit. Representative examples include the reaction of a porphyrin−amine with an *S*-protected alkanethiol bearing an acid chloride,[11] reaction of a porphyrin−amine with the disulfide of an *ω*-mercaptoalkanoic acid,[7] reaction of a porphyrin−bromide with thioacetate[5,9] or thio-

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urea,[13] or conversion of a phthalocyanine−alcohol to the thiol via treatment of the mesylate with thiourea.[8] In this manner, porphyrins bearing one to four thiols have been prepared. Most of these structures have long flexible hydrocarbon chains between the thiol and the porphyrin. A complementary but rarely used route involves introducing the thiol unit into the aldehyde precursor of the porphyrin. One example of this strategy involves the conversion of *p*-(methylthio)benzaldehyde to the *p*-(methylthio)phenyl-substituted porphyrin, which upon Pummerer rearrangement and cleavage afforded the free thiol.[6] The only other examples using this route are described in communications where *S*-acetyl-derivatized thiobenzaldehydes were converted to the corresponding porphyrins, which upon alkaline hydrolysis afforded the free thiols.[4,10] Although undeveloped, this latter route affords the opportunity to prepare porphyrins bearing protected thiols without performing extensive manipulations on the porphyrin. In general, the incorporation of sensitive, bulky, or elaborate substituents in the aldehyde precursor rather than derivatizing the porphyrin has proved to be a very valuable approach, particularly in the synthesis of porphyrin building blocks.[17−19]

We have developed porphyrin building blocks as part of a modular route for synthesizing multiporphyrin arrays.[1,2,20−22] The porphyrin building blocks are employed in defined metalation states, bear substituents that impart solubility, and have iodo and/or ethyne groups as synthetic handles at the periphery. These building blocks are then assembled in a stepwise manner via Pd-coupling reactions to form the diarylethyne-linked array.[23,24] In keeping with this strategy, the synthesis of thiol-derivatized porphyrin monomers requires the introduction of the thiol moiety at the aldehyde stage. To avoid the problems associated with disulfide formation, the thiol is best handled in a protected form. Protecting groups are anticipated to be essential in multiporphyrin arrays bearing multiple thiol units. The development of thiol protecting groups that are compatible with Pd-mediated coupling reactions is an active area of research.[25] Recently Tour et al. reported that an *S*-acetylthio-substituted phenylethynyl oligomer could be deprotected in situ upon exposure to the gold surface.[26] This feature of in situ deprotection was very attractive to us as it enabled handling of the free thiol to be avoided at any stage of the synthesis after forming the protected aldehyde.

In this paper, we have explored a variety of thiol protecting groups in order to identify those that are compatible with porphyrin formation, porphyrin metalation, and Pd-coupling, as well as undergo cleavage in situ on a gold surface. The results concerning behavior of various protecting groups on gold electrodes are important for the design and synthesis of thiol-protected molecular devices. One of our goals is to investigate the fundamental electrochemical properties of porphyrins with different redox potentials and with vertical or horizontal organization on a gold surface. For vertical orientation, we have prepared a family of porphyrins where each porphyrin bears one *S*-protected *p*-thiophenyl group and three electron-withdrawing or electron-releasing substituents at the periphery to tune the electrochemical oxidation potential. For horizontal orientation, a set of porphyrins has been prepared where each porphyrin bears two or four *S*-protected *m*-(thiomethyl)-phenyl groups and one of a variety of central metals for tuning the electrochemical potential. Three porphyrin building blocks have been prepared that bear *S*-protected thiol groups and one or two iodo substituents. This study provides the foundation for preparing diverse thiol-derivatized porphyrin monomers with minimal handling of free thiols.

Results and Discussion

Synthesis of Aldehydes. Our initial synthetic strategy toward monothiol (A_3B) porphyrins for vertical orientation started from 4-methylthiobenzaldehyde which we planned to convert to 4-mercaptobenzaldehyde dimethyl acetal (using the strategy of Young et al.[27]) and next to the thiol-protected dimethyl acetals. The first step involved conversion of the aldehyde group to its dimethyl acetal under standard conditions. The sulfide obtained was successfully converted to the sulfoxide in 95% yield but treatment of the sulfoxide with TFAA led to polymerization rather than affording the free thiol (probably because of cleavage of acetal and intermolecular thioacetalization). We overcame this problem by making two improvements: (1) the dimethyl acetal was replaced by a more bulky acetal protecting group at an earlier stage of the synthesis, (2) milder conditions for the Pummerer

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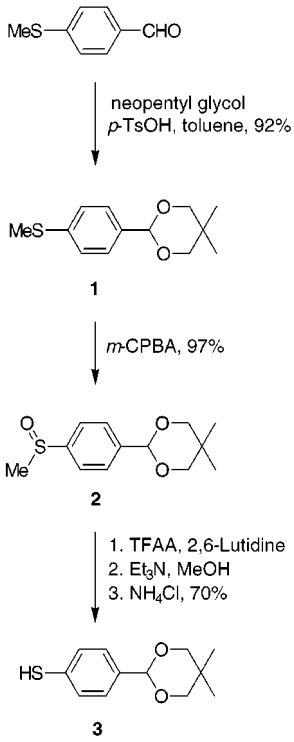
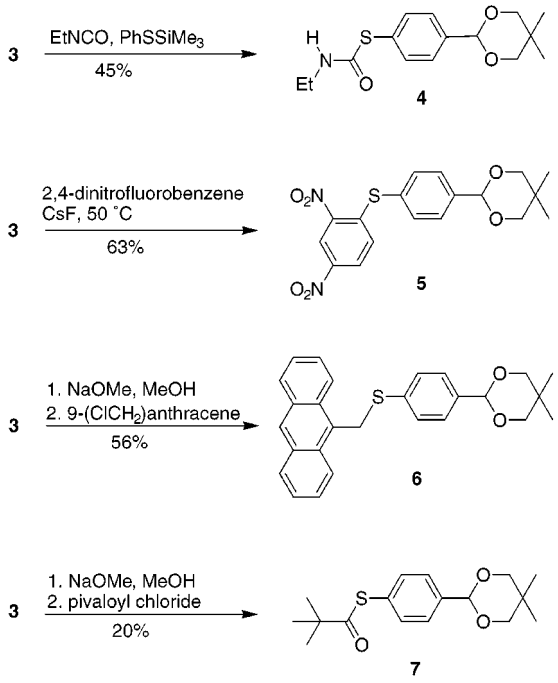
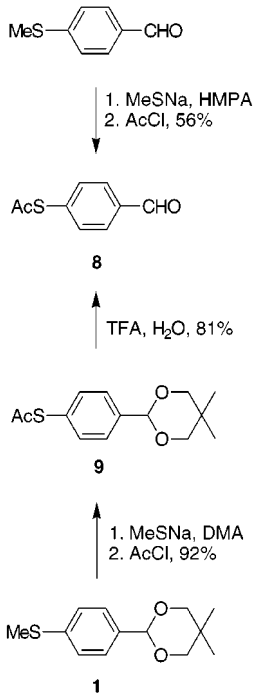
Scheme 1



Scheme 2



Scheme 3



rearrangement were employed.[28] Thus, protection of the formyl group with neopentyl glycol[29] followed by oxidation of the resulting acetal **1** smoothly afforded sulfoxide **2** in 86% overall yield (Scheme 1). Treatment of sulfoxide **2** with TFAA in the presence of 2,6-lutidine followed by hydrolysis of the resulting intermediate furnished thiol **3**. Compound **3** was transformed into the *S*-protected acetals **4**, **5**, **6**, and **7** using ethyl isocyanate,[30] 2,4-dinitrofluorobenzene,[31] 9-chloromethylanthracene,[32] and pivaloyl chloride, respectively, in overall yields of 20−65% from the sulfoxide **2** (Scheme 2). The acetal group in **4**, **5**, **6**, and **7** was selectively hydrolyzed prior to formation of the corresponding porphyrin.

The *S*-acetyl-protected *p*-thiobenzaldehyde **8** was obtained as shown in Scheme 3. *S*-Acetylthiobenzaldehyde **8** was initially prepared in a two-step one-flask procedure. Cleavage of the methyl group of 4-(methylthio)-benzaldehyde according to a general procedure[33] followed by trapping of the resulting thiolate anion with acetyl chloride afforded the desired (*S*-acetylthio)benzaldehyde **8** in 55% yield. The moderate yield and tedious purification of **8** prompted modification of this synthesis. Thus transformation of acetal **1** into **9** according to a general procedure[34] followed by selective TFA-cleavage of the acetal group afforded aldehyde **8** in 68% overall yield (from acetal **1**) without any chromatography.

The thiocyanato-benzaldehyde **10** was prepared according to a general procedure[35] in 20% yield. All attempts to improve the yield by replacement of DMF with 1,3-dimethyl-2-imidazolidinone, increasing the temperature, or prolonging the reaction time were unsuccessful.

Our approach toward horizontally oriented porphyrins required access to *S*-protected *m*-(methylthio)benzalde-

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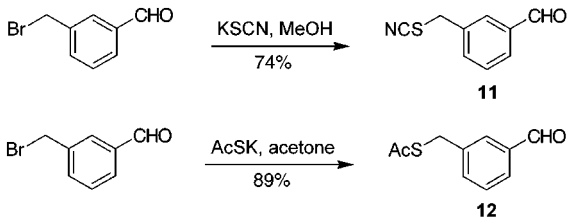
Scheme 4

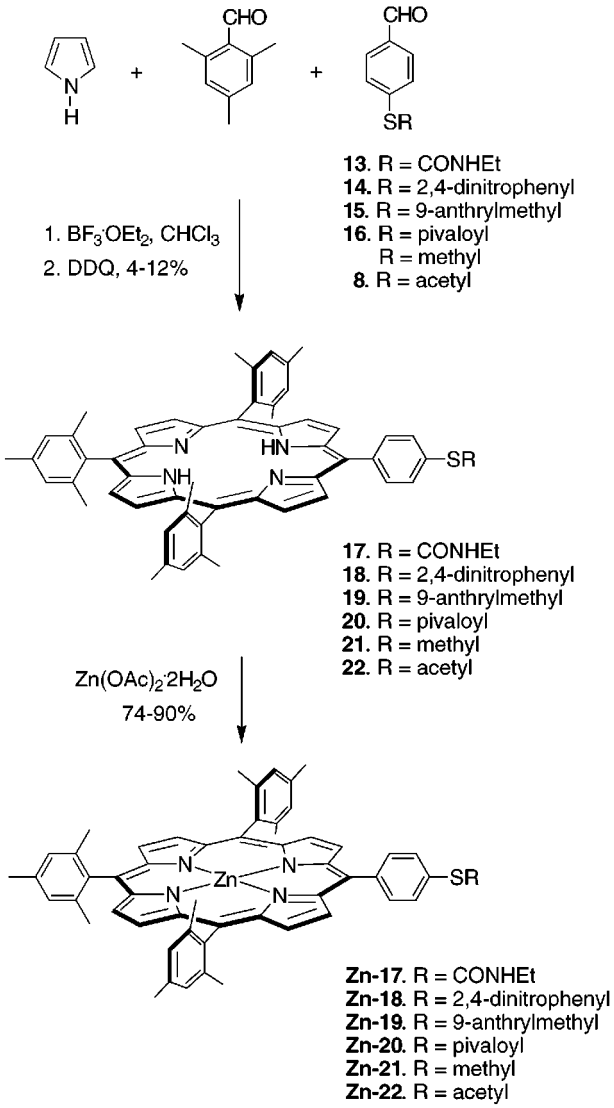


hydes. The commercially available *m*-(bromomethyl)-benzonitrile was reduced with DiBAl-H to the corresponding *m*-(bromomethyl)benzaldehyde.[36] Substitution of the bromide with potassium thiocyanate or potassium thioacetate gave the respective thiocyanatobenzaldehyde **11** or thioacetatobenzaldehyde **12** in good yield (Scheme 4). It is noteworthy that the *S*-cyano and *S*-acetyl protecting groups enabled the protected sulfur unit to be incorporated in one step.

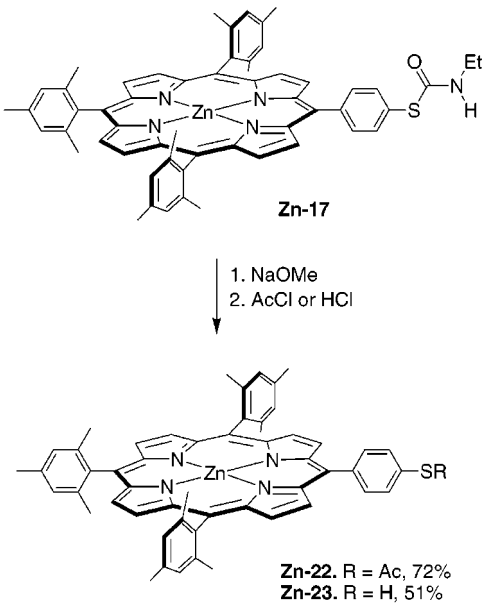
Synthesis of Porphyrins. The investigation of porphyrins oriented in a vertical manner on an electroactive surface can be achieved by the synthesis of porphyrins bearing a *p*-thiophenyl unit at one meso position. The other three meso positions are available for placement of electron-withdrawing or electron-releasing substituents. Such A_3B-porphyrins were prepared using a two-step, one-flask room-temperature synthesis of meso-substituted porphyrins that is compatible with a variety of precursor aldehydes including the ortho-disubstituted benzaldehydes that yield facially encumbered porphyrins.[17,37,38] A mixed-aldehyde condensation of mesitaldehyde, a thiol-protected aldehyde, and pyrrole afforded a mixture of porphyrins, from which the desired thiol-protected A_3B-porphyrin was obtained by chromatography. The acetals **4**−**7** were hydrolyzed with trifluoroacetic acid, and the resulting aldehydes **13**−**16** were used directly without purification in the respective porphyrin syntheses. Thus, aldehydes **8**, **13**, **14**, **15**, or **16** as well as commercially available 4-(methylthio)benzaldehyde afforded thiol-protected A_3B-porphyrins (**17**−**22**) in ∼10% yield (Scheme 5). The corresponding zinc chelates were obtained by reaction with $Zn(OAc)_2 \cdot 2H_2O$ without altering the thiol protecting groups. The similar use of the *p*-thiocyanatobenzaldehyde **10** in a mixed-aldehyde condensation afforded a mixture of porphyrins that could not be separated. This aldehyde was not examined further.

Examination of the behavior of various thiol-protected zinc porphyrins revealed that the *S*-(*N*-ethylcarbamoyl) and *S*-acetyl groups easily cleaved in situ and the resulting porphyrin product bound on the gold surface (vide infra). We decided to confirm this result by also cleaving the *S*-(*N*-ethylcarbamoyl) group in porphyrin **Zn-17** using basic conditions. Treatment of porphyrin **Zn-17** with sodium methoxide followed by acidic workup gave monothiol porphyrin **Zn-23**, which was air-sensitive and proved very difficult to purify to homogeneity (the porphyrin disulfide was also present). The same reaction performed with quenching by acetyl chloride afforded the

Scheme 5



S-acetyl porphyrin **Zn-22**. Both **Zn-17** and **Zn-22** exhibited binding behavior on gold identical to that of the free thiol containing porphyrin **Zn-23**.



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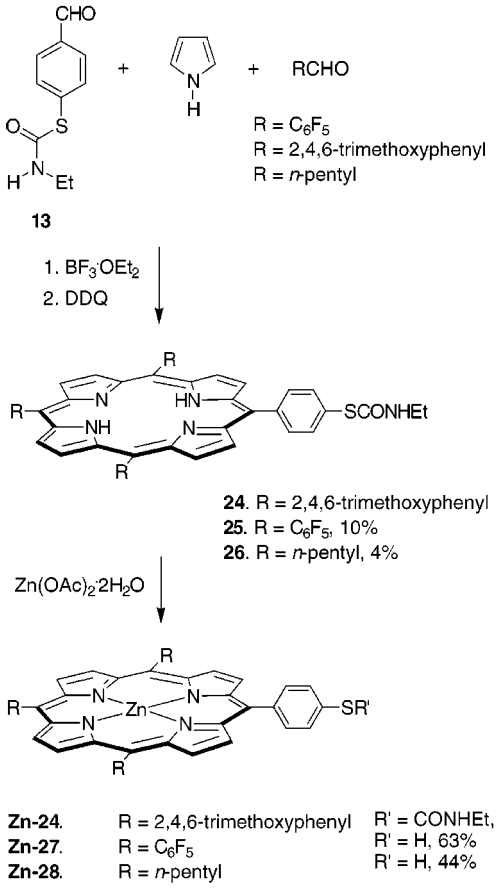
Scheme 6



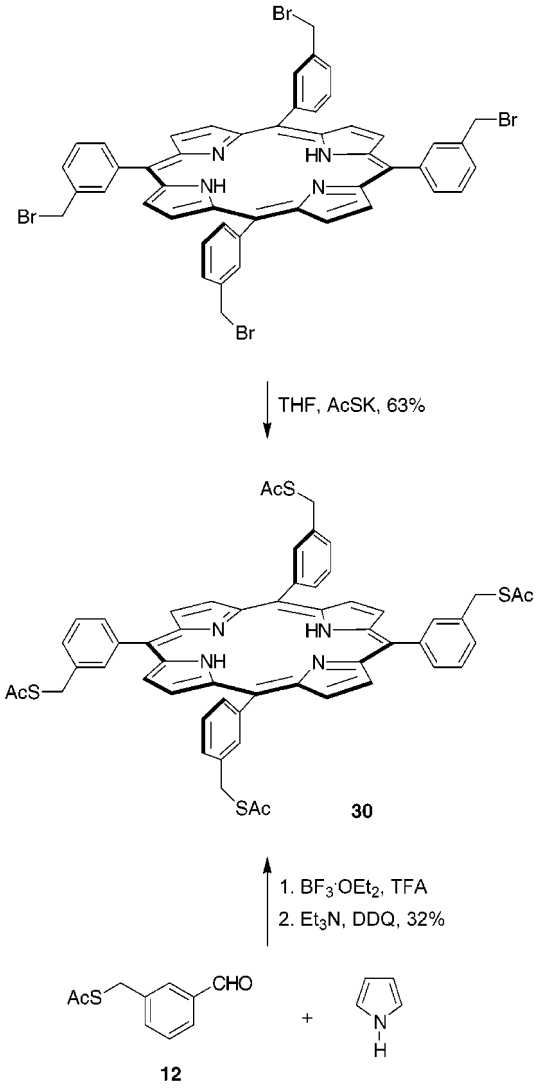
The results of the gold-binding studies (vide infra) prompted us to use the *S*-(*N*-ethylcarbamoyl)-protected thiobenzaldehyde **13** in subsequent syntheses. Thus, mixed aldehyde−pyrrole condensations of aldehyde **13** with 2,4,6-trimethoxybenzaldehyde, pentafluorobenzaldehyde, or *n*-hexanal yielded porphyrin **24**, **25**, or **26**, respectively (Scheme 6). Attempted conversion to the zinc chelate gave the thiol-protected porphyrin **Zn-24**; however, the more forcing conditions required for metalation of the tris(pentafluorophenyl)porphyrin and tri-*n*-pentyl-substituted porphyrin resulted in cleavage of the *S*-(*N*-ethylcarbamoyl) group, giving the free thiol-containing porphyrins **Zn-27** and **Zn-28**.

The investigation of porphyrins oriented in a horizontal manner on an electroactive surface can be achieved by the synthesis of porphyrins bearing a *m*-(mercaptomethyl)phenyl group at each of the four meso positions. We attempted to repeat the synthesis of the unprotected 5,10,15,20-tetrakis[3-(mercaptomethyl)phenyl]porphyrin,[13] but encountered solubility problems due to disulfide formation. Because of the promising results with other thiol protecting groups that resulted in cleavage and binding directly on the gold surface, we decided to synthesize two of the corresponding thiol-protected porphyrins.

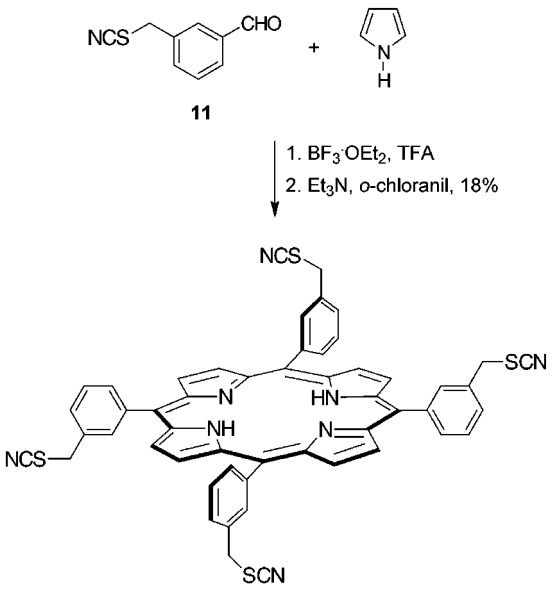
The reaction of **11** with pyrrole at room temperature was performed using new mixed-acid catalysis conditions (TFA + $BF_3{\cdot}OEt_2$) we have recently developed.[39] This approach afforded the desired 5,10,15,20-tetrakis[3-(thiocyanatomethyl)phenyl]porphyrin **29** in 18% yield. Metalation with zinc acetate afforded the

(39) Riggs, J. A.; Lindsey, J. S. Unpublished data.

Scheme 7



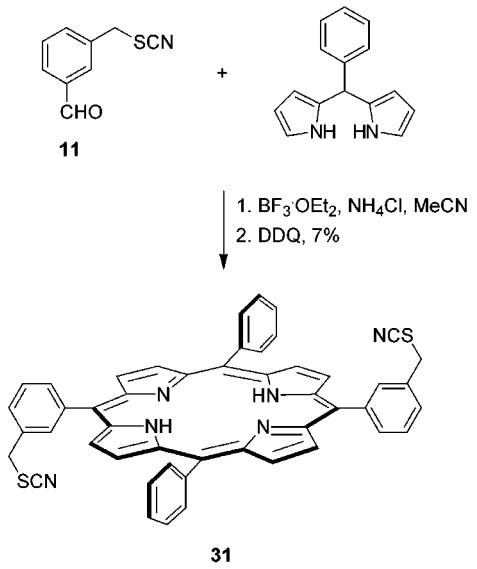
zinc-chelate **Zn-29**. The tetrathiocyanate porphyrin bound on the gold surface in a horizontal orientation (vide infra).



Two routes were examined for the synthesis of 5,10,15,20-tetrakis[3-(*S*-acetylthiomethyl)phenyl]porphyrin **(30)**, as shown in Scheme 7. Substitution of all four bromides in 5,10,15,20-tetrakis[3-(bromomethyl)phenyl)-porphyrin[13,40] with potassium thioacetate afforded **30** in 63% yield. Alternatively, reaction of aldehyde **12** with pyrrole at room temperature using the mixed acid catalysis conditions[39] gave **30** in 32% yield.

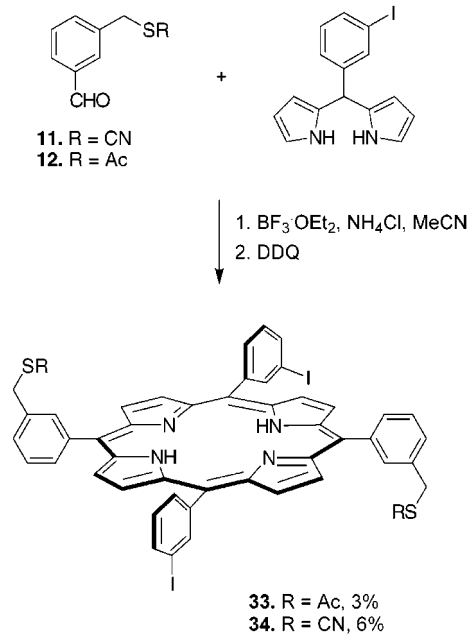
A range of electrochemical potentials was achieved with the horizontally oriented porphyrins by metalation of 5,10,15,20-tetrakis[3-(*S*-acetylthiomethyl)phenyl]porphyrin **(30)** with various metal salts. Metalation of free base porphyrin **30** with $Zn(OAc)_2 \cdot 2H_2O$, $Co(OAc)_2 \cdot 4H_2O$, $Cu(OAc)_2 \cdot H_2O$, or $AgNO_3$/triethylamine gave the corresponding metalloporphyrin (**Zn-30**, **Co-30**, **Cu-30** or **Ag-30**) without alteration of the *S*-acetyl protecting groups.

Driven by these positive results, we decided to synthesize a porphyrin with only two groups for attachment to the gold surface. Condensation of aldehyde **11** with 5-phenyldipyrromethane[41] using $BF_3 \cdot OEt_2$ in acetonitrile to minimize scrambling[42] gave the desired *trans*-porphyrin **31** in 7% yield. This product was accompanied by 10,15,20-triphenyl-5-[3-(thiocyanatomethyl)phenyl]porphyrin in 2% yield due to scrambling. Metalation of **31** with zinc acetate afforded the zinc porphyrin **Zn-31** in 59% yield. Porphyrin **Zn-31** also bound to the gold surface.

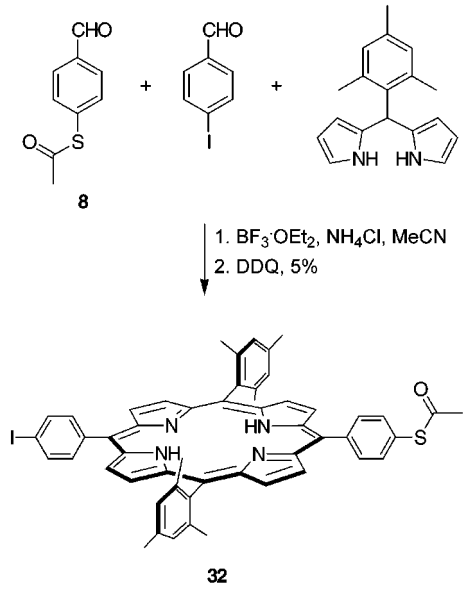


We next turned to the preparation of porphyrin building blocks for the synthesis of multiporphyrin arrays that can be attached to an electroactive surface. Porphyrins bearing iodophenyl groups are versatile synthetic units for the preparation of a wide variety of multiporphyrin arrays in linear,[20] star,[21] cyclic,[22] and dendritic[2] architectures. We prepared a porphyrin bearing one iodophenyl group and one *S*-protected *p*-thiophenyl unit in a trans orientation. This porphyrin can be used for vertical organization via single-site attachment of a multiporphyrin array on an electroactive surface. The synthesis

Scheme 8



was performed by mixed aldehyde condensation of *S*-acetyl-protected *p*-thiobenzaldehyde **9**, *p*-iodobenzaldehyde, and 5-mesityldipyrromethane. The three expected porphyrin products were separated by chromatography, affording the desired *trans*-porphyrin **32** in 4.9% yield.



We also prepared porphyrins bearing two *m*-iodophenyl groups and two *S*-protected *m*-(thiomethyl)phenyl units in a trans orientation. These porphyrins can be used for horizontal organization via two-site attachment of a multiporphyrin array on an electroactive surface. Thus, the condensation of *S*-acetyl-protected benzaldehyde **12** and 5-(3-iodophenyl)dipyrromethane resulted in a small amount of scrambling, as is typical with unhindered dipyrromethanes.[42] The desired *trans*-porphyrin **33** was obtained by chromatography in 3% yield (Scheme 8). Porphyrin **34** was prepared in a similar manner from the thiocyanatobenzaldehyde **11** in 6% yield.

Characterization of Porphyrins. The protected-thiol porphyrins were stable under routine handling. The

(40) Karaman, R.; Blaskó, A.; Almarsson, Ö.; Arasasingham, R.; Bruice, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 4889−4898.

(41) (a) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440. (b) Littler, B. J.; Miller, M. A.; Hung C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.

(42) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.

porphyrins were characterized by TLC, ^{1}H NMR (with the exception of the paramagnetic **Co-30**, **Cu-30** and **Ag-30**), LD-MS, FAB-MS, and UV/vis spectroscopy. Fluorescence emission and excitation spectroscopy were used to confirm the completeness of the different metalation procedures.

Generally, the LD-MS spectrum of a porphyrin shows the molecule ion peak M^+ in high intensity with only little fragmentation.[43] However, some porphyrins with delicate peripheral groups undergo characteristic and extensive fragmentation upon LD-MS analysis. Of the six thiol protecting groups examined, all but the 2,4-dinitrophenyl group exhibited significant fragmentation. For example, porphyrins with thiocyanate substituents show the loss of the cyano and the thiocyanato groups, with the latter exhibiting more intense peaks. If more than one thiocyanate group is present, fragmentation can occur for each of these groups. Porphyrins with *S*-acetyl groups show loss of both the acetyl ($-COCH_3$) and the thioacetate ($-SCOCH_3$) groups. Such fragmentation can generally occur for each thioacetate substituent. A further LD-MS feature observed with thioacetate-derivatized porphyrins involves the appearance of an $(M + 15)^+$ peak. Because this peak occurred in the LD-MS spectra of all porphyrins with thioacetate substituents, which were synthesized via different routes, and no other types of spectra show any evidence for the presence of another species, this cannot be an impurity but must be a laser photolysis artifact involving the transfer of a methyl group. In each case, the $(M + 15)^+$ peak exhibited the same pattern of fragmentation as observed for the parent molecule ion (M^+). The intensity of the $(M + 15)^+$ peak is about 10% of that of the M^+ peak. In general, each protecting group exhibited a characteristic fragmentation pattern and did not interfere with identification of the porphyrin.

Behavior of the Porphyrins on Gold. We surveyed the behavior of the thiol-protected zinc chelates **Zn-17**−**Zn-22** on gold electrodes. These studies revealed that the *S*-(*N*-ethylcarbamoyl) (**Zn-17**) and *S*-acetyl (**Zn-22**) groups were easily cleaved on the gold surface, whereas the *S*-(2,4-dinitrophenyl) (**Zn-18**), *S*-(9-anthrylmethyl) (**Zn-19**), *S*-pivaloyl (**Zn-20**), and *S*-methyl (**Zn-21**) protecting groups were not cleaved. For these groups where no cleavage occurred, the thiol-protected porphyrins were not bound to the gold surface. We found that **Zn-17** (*S*-(*N*-ethylcarbamoyl) protected), **Zn-22** (*S*-acetyl protected), and **Zn-23** (free thiol) afforded products that bound to the gold surface identically. The thiocyanatomethyl-derivatized porphyrins (**Zn-29**, **Zn-31**) bound to the gold electrode, though in this case, our current data are insufficient to determine whether the bound species is a thiol (cleavage and binding) or a thiocyanate (binding only). A full description of these studies, including results from electrochemistry and surface spectroscopy, will be published elsewhere.[44] These results are in accord with and extend the report of Tour et al. that the *S*-acetyl group of various thiol-substituted arenes (not porphyrins) is cleaved on the gold surface.[26] These results are summarized in Table 1.

Compatibility of the Protecting Groups with Pd-Coupling Reactions. For the synthesis of multiporphyrin arrays, we developed a refined Pd-coupling method that proceeds under mild conditions and is compatible with diverse free base and metalloporphyrins.[23,24] To check if the various thiol protecting groups are compatible with these conditions, screening experiments were done. The Pd-coupling of zinc(II)−5-(*p*-ethynylphenyl)-10,15,20-trimesitylporphyrin[23] with zinc(II)−5-(*p*-iodophenyl)-10,15,20-trimesitylporphyrin[18] was examined in the presence of an equimolar amount of an appropriate thiol-protected aldehyde or acetal. The results were monitored by analytical SEC (HPLC). These screening tests showed that the *S*-cyano and the *S*-(*N*-ethylcarbamoyl) groups are incompatible with the Pd-coupling conditions, while the *S*-acetyl or *S*-pivaloyl groups did not interfere with the Pd-coupling reaction. These results were confirmed by Pd-coupling with a zinc porphyrin bearing two iodo and two *S*-cyano groups (**Zn-34**), where no porphyrin trimer was formed.[45] Complexation of the nitrogen atoms of the thiocyanates with Pd and formation of a precipitate has been observed under different conditions.[46] In contrast, the Pd-coupling of a porphyrin bearing two iodo and two *S*-acetyl groups (**Zn-33**) afforded the expected trimer in good yield.[45] These results are summarized in Table 1. The use of these and related porphyrin building blocks in the synthesis of multiporphyrin arrays with protected thiol groups at specific sites, and the electrochemical properties of the arrays on electroactive surfaces, will be reported in due course.

Table 1. Evaluation of Thiol Protecting Groups

R	porphyrin formation[a]	metalation (Zn)[b]	binding on Au[c]	Pd-coupling reaction[d]
3-($RSCH_2$)phenyl				
S-cyano	yes	yes	yes	no[e]
S-acetyl	yes	yes	yes[f]	yes[g]
4-(RS)phenyl				
S-acetyl	yes	yes	yes[f]	NE[h]
S-(*N*-ethylcarbamoyl)	yes	yes	yes[f]	no[i]
S-cyano	yes	yes	yes	NE[h]
S-(9-anthrylmethyl)	yes	yes	no	NE[j]
S-(2,4-dinitrophenyl)	yes	yes	no	NE[j]
S-pivaloyl	yes	yes	no	yes[k]

[a] Porphyrin formation was assessed using the two-step one-flask synthesis at or near room temperature. [b] Metalation was performed using zinc acetate in methanolic $CHCl_3$ or CH_2Cl_2 at room temperature. [c] Binding on gold was assessed by exposure of the porphyrin solution to the gold surface followed by electrochemical examination. [d] Pd-coupling reactions were assessed by a screening reaction in the presence of an appropriate *S*-protected thiobenzaldehyde or acetal (as well as by the coupling of an iodo porphyrin and an ethynyl porphyrin). [e] Examined using **11**. [f] Cleavage of the protecting group and binding of the resulting thiol to gold. [g] Examined using **12**. [h] Not examined due to results with the same protecting group at the 3-position. [i] Examined using **4** and **13**. [j] Not examined due to lack of any binding on gold. [k] Examined using **7**.

Conclusions

The introduction of a protected thiol unit in an aldehyde enables the corresponding porphyrin to be prepared without handling free porphyrin thiols. One set of porphyrins has been prepared for vertical organization via

(43) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291.
(44) Roth, K. M.; Gryko, D. T.; Clausen, C.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. Manuscript in preparation.
(45) Clausen, C.; Lindsey, J. S. Manuscript in preparation.
(46) Davis, R. C.; Grinter, T. J.; Leaver, D.; O'Neil, R. M.; Thomson, G. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2881−2887.

one linker, and a second set has been prepared for horizontal organization via two or four linkers on an electroactive surface. The *S*-(*N*-ethylcarbamoyl) protecting group has been identified to undergo cleavage in situ on gold electrodes, a phenomenon previously recognized only for the *S*-acetyl group. The *S*-cyano group results in binding (if not cleavage) on the gold surface. These three protecting groups can be used in the synthesis of monomeric porphyrins for attachment to an electroactive surface. Conversely, the *S*-(9-anthrylmethyl), *S*-(2,4-dinitrophenyl), and *S*-pivaloyl groups do not afford a bound species upon exposure to gold. Among the groups that do undergo cleavage, only the *S*-acetyl group is compatible with the Pd-coupling reactions employed in the synthesis of diarylethyne-linked multiporphyrin arrays.

Experimental Section

General Methods. All chemicals obtained commercially were used as received unless otherwise noted. Reagent-grade solvents (CH_2Cl_2, $CHCl_3$, hexanes) and HPLC-grade solvents (acetonitrile, toluene) were used as received from Fisher. Pyrrole was distilled from CaH_2. All reported NMR spectra were obtained at 300 MHz in $CDCl_3$. UV−vis absorption and fluorescence spectra were recorded in CH_2Cl_2 or toluene as described previously.[21,22] Flash chromatography was performed on flash silica (Baker, 200−400 mesh) or alumina (Fisher, 80−200 mesh). Mass spectra were obtained via laser desorption (LD-MS) in the absence of an added matrix,[47] fast atom bombardment (FAB-MS, 10 ppm elemental compositional accuracy for the porphyrins), or electron-impact mass spectrometry (EI-MS). Porphyrin metalation was monitored by fluorescence excitation and emission spectroscopy.

Characterization of the Porphyrins on Gold Electrodes. Glass slides with gold electrodes 75 μm in width were stored under dry ethanol until use. The slides were dried with a stream of nitrogen prior to exposure to a porphyrin solution. Exposure of the porphyrin solution (0.1 mg/mL in absolute ethanol) was performed at room temperature for several hours (at which point no further change was observed in monolayer properties). The slide was then rinsed with dry ethanol. The gold electrode was then examined by cyclic voltammetry in order to establish the presence of a self-assembled porphyrin monolayer. This approach also enabled the extent of coverage of the monolayer on the gold surface to be determined. Thiol-derivatized porphyrins that do not bind to the gold surface do not exhibit a characteristic electrochemical response. Control compounds were provided by the *p*-(methylthio)phenyl substituted porphyrin **Zn-21**, which does not bind to the gold electrode, and the analogous *p*-mercaptophenyl substituted porphyrin **Zn-23**, which does bind to the gold electrode. (For clarification of the conflicting results concerning formation of self-assembled monolayers from thiols and sulfides, see Jung et al.[48]) A detailed description of the fabrication of the gold electrodes, deposition procedures, and electrochemical results will be published elsewhere.[44]

2-[4-(Methylthio)phenyl]-5,5-dimethyl-1,3-dioxane (1). Samples of 4-(methylthio)benzaldehyde (20.0 mL, 150 mmol), neopentyl glycol (16.0 g, 155 mmol), toluene (250 mL), and *p*-toluenesulfonic acid (190 mg, 1.00 mmol) were placed in a 500 mL flask fitted with a Dean−Stark trap and a reflux condenser. The mixture was refluxed cautiously until a sudden exotherm ceased and then for an additional hour (total ∼1.5 h). The cooled mixture was washed with $NaHCO_3$ solution and with water. After drying with Na_2SO_4 and evaporation, crystallization from hexanes afforded white crystals (33.1 g, 92.0%): mp 74−75 °C; ^{1}H NMR δ 0.83 (s, 3H), 1.33 (s, 3H), 2.50 (s, 3H), 3.67 (AB/2, 2H, J = 10.2 Hz), 3.79 (AB/2, 2H, J = 10.2 Hz), 5.25 (s, 1H), 7.30, (AA′BB′, 4H); ^{13}C NMR δ 16.5, 22.6, 23.8, 30.9, 78.3, 102.1, 127.1, 127.4, 136.2, 140.0; EI-MS m/z 238.1028 $(M)^+$ ($C_{13}H_{18}O_2S$ requires 238.1028). Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; S, 13.45; Found: C, 65.62; H, 7.70; S, 13.55.

2-[4-(Methylsulfoxy)phenyl]-5,5-dimethyl-1,3-dioxane (2). A solution of acetal **1** (19 g, 80 mmol) in CH_2Cl_2 (150 mL) was cooled to −20 °C and stirred vigorously. Then a solution of *m*-CPBA (31 g of 50−55% water suspension, 90 mmol) in CH_2Cl_2 (100 mL) was added dropwise over 1 h. The mixture was stirred at 0 °C for an additional 1 h. Then $Ca(OH)_2$ (11 g, 0.15 mmol) and Na_2SO_4 (20 g) were added, and stirring was continued for 1 h. After filtration and evaporation, the warm colorless oil was dissolved in CH_2Cl_2 (20 mL) and hexanes was added, affording white crystals that were isolated by filtration (14.6 g). The filtrate was evaporated, and the residual oil was recrystallized, affording a second crop of white crystals. The total yield was 19.6 g (97%): mp 116−117 °C; ^{1}H NMR δ 0.77 (s, 3H), 1.24 (s, 3H), 2.65 (s, 3H), 3.62 (AB/2, 2H, J = 11.1 Hz), 3.74 (AB/2, 2H, J = 10.8 Hz), 5.40 (s, 1H), 7.6−7.7 (m, 4H); ^{13}C NMR δ 22.5, 23.7, 30.9, 44.7, 78.3, 101.3, 124.0, 128.0, 142.2, 146.7; EI-MS obsd 254.0975, calcd exact mass 254.0977 ($C_{13}H_{18}O_3S$). Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13; S, 12.61. Found: C, 61.29; H, 7.03; S, 12.70.

2-(4-Mercaptophenyl)-5,5-dimethyl-1,3-dioxane (3). Sulfoxide **2** (7.62 g, 30.0 mmol) was dissolved in acetonitrile (120 mL). 2,6-Lutidine (10.8 mL, 93.0 mmol) was added, and the mixture was cooled to −20 °C. To the resulting suspension was added TFAA (12.7 mL, 90.0 mmol) dropwise, maintaining the temperature below 0 °C. The precipitate disappeared, and the mixture turned a lemon yellow. When the addition was complete, the mixture was stirred at −10 to 0 °C for 1 h and then allowed to warm to room temperature. All volatile materials were evaporated at 30 °C. Next, a precooled (0 °C) mixture of triethylamine (50 mL) and methanol (50 mL) was added. After 30 min at room temperature, all volatile materials were evaporated under reduced pressure at low temperature. The residual yellow oil was dissolved in ethyl ether (70 mL) and extracted with saturated NH_4Cl (250 mL). The layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated to dryness giving a yellow-orange oil (6.61 g, 98% yield of crude material) of which ∼70% was the desired compound (^{1}H NMR analysis). The crude thiol was pure enough for the next step. A small sample was oxidized to the respective disulfide and characterized: mp 134−136 °C; ^{1}H NMR δ 0.80 (s, 3H), 1.28 (s, 3H), 3.63 (AB/2, 2H, J = 10.2 Hz), 3.76 (AB/2, 2H, J = 11.2 Hz), 5.36 (s, 1H), 7.43, 7.49 (AA′BB′, 4H); ^{13}C NMR δ 16.5, 22.6, 23.7, 30.9, 78.3, 101.8, 127.6, 128.1, 138.2, 138.4; FAB-MS obsd 446.1574, calcd exact mass 446.1586 ($C_{24}H_{30}O_4S_2$). Anal. Calcd for $C_{24}H_{30}O_4S_2$: C, 64.54; H, 6.77; S, 14.36. Found: C, 64.52; H, 6.70; S, 14.44.

2-[4-[*S*-(*N*-Ethylcarbamoyl)thio]phenyl]-5,5-dimethyl-1,3-dioxane (4). To the crude thiol **3** (6.60 g, 29.5 mmol) was added ethyl isocyanate (2.33 mL, 29.5 mmol) followed by phenylthiotrimethylsilane (0.568 mL, 3.00 mmol). The reaction mixture was stirred for 3 h at room temperature. During this time, the mixture gradually solidified to a pale yellow solid. Then *n*-pentane (5 mL) was added, and the suspension was filtered and washed thoroughly with *n*-pentane. The yellowish crystals were dissolved in hot toluene, and hexanes was added. After standing for a few hours at room temperature, off-white crystals were collected (4.01 g, yield 45.2% from sulfoxide **2**): mp 117−118 °C; ^{1}H NMR δ 0.81 (s, 3H), 1.08 (t, 3H, J = 7.2 Hz), 1.29 (s, 3H), 3.2−3.3 (m, 2H), 3.67 (AB/2, 2H, J = 10.8 Hz), 3.78 (AB/2, 2H, J = 11.1 Hz), 5.42 (s, 1H), 5.57 (br s, 1H), 7.58 (br s, 4H); ^{13}C NMR δ 15.5, 22.6, 23.7, 30.9, 37.2, 78.3, 101.5, 128.1, 130.0, 136.0, 140.7, 166.4; EI-MS obsd 295.1235, calcd exact mass 295.1242 ($C_{15}H_{21}NO_3S$). Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74; S, 10.86. Found: C, 61.16; H, 7.05; N, 4.70; S, 11.02.

2-[4-[*S*-(2,4-Dinitrophenyl)thio]phenyl]-5,5-dimethyl-1,3-dioxane (5). Crude thiol **3** (1.00 g, 4.46 mmol) was mixed with 2,4-dinitrofluorobenzene (830 mg, 4.46 mmol). After the mixture was heated to 35 °C, cesium fluoride (1.35 g, 8.92

(47) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99.
(48) Jung, C.; Dannenberger, O.; Xu, Y.; Buck, M.; Grunze, M. *Langmuir* **1998**, *14*, 1103−1107.

mmol) was added. The yellow mixture was stirred and heated at 45 °C for 1 h. Next, toluene (10 mL) was added, and the hot suspension was filtered to remove insoluble materials. The filtrate was evaporated to dryness, giving an orange oil. The crude product was chromatographed on silica (CH_2Cl_2/hexanes, 1:2), affording a yellow oil that finally was crystallized from hot ethanol, affording yellow crystals (1.2 g, 63% from sulfoxide **2**): mp 132−133 °C; ^{1}H NMR δ 0.77 (s, 3H), 1.24 (s, 3H), 3.63 (AB/2, 2H, J = 10.8 Hz), 3.74 (AB/2, 2H, J = 11.1 Hz), 5.40 (s, 1H), 6.93 (d, 1H, J = 8.7 Hz), 7.57 (AA′BB′, 4H), 8.00 (dd, 1H, J = 8.7 Hz, J = 2.1 Hz), 8.99 (d, 1H, J = 2.1 Hz); ^{13}C NMR δ 22.4, 23.6, 30.9, 78.4, 101.2, 122.0, 127.5, 129.2, 129,6, 130.0, 136.4, 142.2, 144.9, 148.8; EI-MS obsd 390.0873, calcd exact mass 390.0886 ($C_{18}H_{18}N_2O_6S$). Anal. Calcd for $C_{18}H_{18}N_2O_6S$: C, 55.38; H, 4.65; N, 7.18; S, 8.21. Found: C, 55.50; H, 4.64; N, 7.12; S, 8.30.

2-[4-[*S*-(9-Anthrylmethyl)thio]phenyl]-5,5-dimethyl-1,3-dioxane (6). Crude thiol **3** (1.15 g, 50.0 mmol) was dissolved in methanol (10 mL). To this solution was added a freshly prepared solution of sodium methoxide [from Na (117 mg, 50.0 mmol) and methanol (20 mL)]. After 15 min, the mixture was evaporated to dryness and the orange solid was dried under vacuum. Then the solid was dissolved in anhydrous DMF (15 mL) at room temperature and a solution of 9-chloromethylanthracene (1.13 g, 50.0 mmol) in DMF (10 mL) was added. The reaction mixture was stirred at room temperature for 72 h. The DMF was evaporated under reduced pressure, and the resulting yellow oil was chromatographed on alumina (hexanes/CH_2Cl_2). The resulting yellow crystals were recrystallized from CH_2Cl_2/hexanes to afford 1.17 g of the desired product (56.4% from sulfoxide **2**): mp 158−159 °C; ^{1}H NMR δ 0.84 (s, 3H), 1.37 (s, 3H), 3.69 (AB/2, 2H, J = 10.8 Hz), 3.84 (AB/2, 2H, J = 10.8 Hz), 5.01 (s, 2H), 5.44 (s, 1H), 7.4−7.6 (m, 8H), 8.01, 8.26 (AA′BB′, 4H), 8.42 (s, 1H); ^{13}C NMR δ 22.6, 23.8, 30.9, 32.7, 78.4, 102.0, 124.8, 125.8, 127.1, 127.6, 128.1, 128.5, 129.7, 129.9, 130.8, 132,2, 137.5, 139.3; FAB-MS obsd 414.1653, calcd exact mass 414.1654 ($C_{27}H_{26}O_2S$). Anal. Calcd for $C_{27}H_{26}O_2S$: C, 78.22; H, 6.32; S, 7.73. Found: C, 78.05; H, 6.24; S, 7.63.

2-[4-(*S*-Pivaloylthio)phenyl]-5,5-dimethyl-1,3-dioxane (7). Crude thiol **3** (2.24 g, 8.82 mmol) was dissolved in CH_2Cl_2 (10 mL), and methanol (10 mL) was added. To this solution was added a freshly prepared solution of sodium methoxide [from Na (230 mg, 10.0 mmol) and methanol (5 mL)]. After 30 min, pivaloyl chloride (1.40 mL, 11.4 mmol) was added, and the mixture was stirred for an additional 3 h at room temperature. After evaporation of all volatile components, the residual oil was chromatographed (silica, CH_2Cl_2), affording a mixture of less polar compounds. The yellowish oil was further purified using centrifugal preparative chromatography (silica, CH_2Cl_2/hexanes, 1:1) to afford a mixture of the title compound and the corresponding disulfide. The mixture was dissolved in CH_2Cl_2, and methanol was added. Next, CH_2Cl_2 was flushed out with argon. The crystals were filtered and dissolved in hot methanol and the mixture was carefully cooled. After 30 min, crystals of the title compound were collected (502 mg, 19.8% from sulfoxide **2**): mp 115−116 °C; ^{1}H NMR δ 0.80 (s, 3H), 1.28 (s, 3H), 1.32 (s, 9H), 3.64 (AB/2, 2H, J = 10.2 Hz), 3.77 (AB/2, 2H, J = 10.2 Hz), 5.41 (s, 1H), 7.40, 7.55 (AA′BB′, 4H); ^{13}C NMR δ 22.6, 23.7, 28.1, 30.9, 47.6, 78.3, 101.6, 127.5, 129.3, 135.4, 140.1. Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84; S, 10.40. Found: C, 66.22; H, 7.92; S, 10.60.

4-(*S*-Acetylthio)benzaldehyde (8). Method I. 4-(Methylthio)benzaldehyde (4.45 mL, 0.033 mol) and sodium thiomethoxide (10 g, 0.143 mol) were suspended in HMPA (100 mL), and the reaction mixture was heated with stirring at 100 °C for 18 h. The resulting brown suspension was cooled, and acetyl chloride (10.2 mL, 0.143 mol) was added. After 2 h, the resulting suspension was poured into water, and ethyl ether was added. The ethereal layer was extracted with water three times, dried, and evaporated. Next, chromatography was performed (silica, CH_2Cl_2/hexanes, 1:1). A yellow oil was collected containing the title compound with some impurities (3.33 g, crude yield 55.5%). This oil was recrystallized from ethanol giving off-white crystals (1.05 g, 18.3%). **Method II.** Acetal **9** (7.0 g, 0.027 mol) was suspended in water (4 mL), and TFA (13 mL) was added. The resulting orange solution was allowed to stand overnight and then poured into water and extracted with toluene. The organic layer was washed extensively with water, dried, and evaporated. The brown residue was distilled under reduced pressure (120 °C, 0.01 mmHg) to obtain a light orange oil. After dissolution in ethanol, addition of seed crystals and cooling afforded light orange crystals. Careful evaporation of this suspension at room temperature afforded 3.8 g (81%): mp 44−45 °C (lit.[49] mp 46 °C); ^{1}H NMR δ 2.44 (s, 3H), 7.56 (AA′BB′, 2H), 7.87 (AA′BB′, 2H), 10.00 (s, 1H); ^{13}C NMR δ 31.2, 130.6, 135.2, 136.1, 137.1, 192.1, 192.9; EI-MS obsd 180.0252 $(M)^+$, calcd exact mass 180.0245. Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47; S, 17.79. Found: C, 59.58; H, 4.52; S, 17.78.

2-[4-(*S*-Acetylthio)phenyl]-5,5-dimethyl-1,3-dioxane (9). Sodium thiomethoxide (10.0 g, 0.143 mol) and acetal **1** (6.80 g, 29 mmol) were suspended in *N*,*N*-dimethylacetamide (125 mL), and the mixture was heated at 140 °C overnight. The resulting orange, turbid solution was cooled and acetyl chloride (10.2 mL, 0.143 mol) was added dropwise. The light orange suspension was then poured into water and extracted with ethyl ether. The ethereal layer was washed with water, dried, and evaporated. The resulting oil was distilled under reduced pressure (140−160 °C, 0.01 mmHg) to obtain light orange crystals (7.0 g, 92%): mp 88−90 °C; ^{1}H NMR δ 0.81 (s, 3H), 1.30 (s, 3H), 2.41 (s, 3H), 3.66 (AB/2, 2H, J = 10.2 Hz), 3.79 (AB/2, 2H, J = 10.2 Hz), 5.42 (s, 1H), 7.44, 7.58 (AA′BB′, 4H); ^{13}C NMR δ 22.6, 23.8, 30.9, 30.9, 78.3, 101.6, 127.7, 129.2, 135.0, 140.5, 194.4; EI-MS obsd 266.0979 $(M)^+$, calcd exact mass 266.0977 ($C_{14}H_{18}O_3S$).

4-Thiocyanatobenzaldehyde (10). Under an argon atmosphere, a mixture of 4-iodobenzaldehyde (232 mg, 1.00 mmol), KSCN (95.0 mg, 1.00 mmol), CuSCN (120 mg, 1.00 mmol), and DMF (7.5 mL) was heated with stirring in an oil bath at 140 °C for 12 h. After cooling, the mixture was diluted with toluene and water and then filtered through a Celite pad. The aqueous phase was extracted with toluene, and the organic fractions were combined and washed with water, dried, and concentrated. The resulting dark oil was purified using centrifugal preparative chromatography (silica, CH_2Cl_2/hexanes, 1:2) to obtain off-white crystals (33 mg, 20%): mp 82−83 °C; ^{1}H NMR δ 7.63, 7.92 (AA′BB′, 2H), 10.01 (s, 1H); ^{13}C NMR δ 109.4, 129.3, 131.6, 132.9, 191.3; EI-MS obsd 163.0092, calcd exact mass 163.0092 (C_8H_5NOS). Anal. Calcd for C_8H_5NOS: C, 58.88; H, 3.09; N, 8.58; S, 19.65. Found: C, 58.85; H, 2.99; N, 8.61; S, 19.68.

3-(Thiocyanatomethyl)benzaldehyde (11). To a solution of 3-(bromomethyl)benzaldehyde[36] (300 mg, 1.5 mmol) in methanol (5 mL) was added a solution of potassium thiocyanate (321 mg, 3.3 mmol) in methanol (4 mL) under stirring at room temperature. After a few minutes, a precipitate formed. The reaction was monitored by TLC and stopped by adding water (20 mL) when no starting material was detectable. Ethyl ether (30 mL) was added, and the phases were separated. The aqueous phase was washed twice with ethyl ether (20 mL), and the combined organic phases were dried (Na_2SO_4). Column chromatography over flash silica gel (ethyl ether/hexanes, 1:2) gave 198 mg (74% yield) of a slightly yellow oil that solidified upon standing at 0 °C. Recrystallization (ethyl ether/hexanes) gave colorless crystals (mp 39 °C): IR (neat) $\tilde{\nu}$ 3060, 2996, 2832, 2149, 1695, 1603; ^{1}H NMR δ 4.22 (s, 2H), 7.55−7.69 (m, 2H), 7.86−7.93 (m, 2H), 10.04 (s, 1H); ^{13}C NMR (APT) δ 32.7 (+), 111.4 (+), 129.6 (−), 129.8 (−), 130.1 (−), 134.6 (−), 135.7 (+), 136.8 (+), 191.4 (−); GC−MS (EI) obsd 177, 149, 120, 119, 91. Anal. Calcd for C_9H_7NOS: C, 60.99; H, 3.98; N, 7.90; S, 18.09. Found: C, 60.75; H, 4.05; N, 7.86; S, 18.19.

3-(*S*-Acetylthiomethyl)benzaldehyde (12). To a solution of 3-(bromomethyl)benzaldehyde[36] (3.156 g, 15.9 mmol) in

(49) Zhdanov, Y. A.; Minkin, V. I.; Olekhnovich, L. P.; Malysheva, E. N. *Zh. Org. Khim.* **1970**, *6*, 554−559, *Engl. Transl.* **1970**, *6*, 551−555.

acetone (50 mL) was added potassium thioacetate (2.180 g, 19.1 mmol) under stirring at room temperature. Then the mixture was refluxed. After a few minutes, a precipitate formed. The reaction was monitored by TLC and cooled to room temperature after 4 h when no starting material was detectable. Water (60 mL) was added, and the mixture was extracted four times with ethyl ether (50 mL). The combined organic phases were dried (Na_2SO_4). Column chromatography over flash silica gel (ethyl ether/hexanes, 1:3) gave 2.736 g (89% yield) of a yellow oil that darkened upon standing (nonetheless, elementary analysis 7 weeks after exposure to air at room temperature indicated a high level purity as listed below): IR (neat) $\tilde{\nu}$ 3062, 2835, 2732, 1694, 1603, 1588; ^{1}H NMR δ 2.24 (s, 3H), 4.06 (s, 2H), 7.31−7.39 (m, 1H), 7.43−7.49 (m, 1H), 7.61−7.71 (m, 2H), 9.87 (s, 1H); ^{13}C NMR (APT) δ = 29.9 (−), 32.4 (+), 128.3 (−), 129.0 (−), 129.5 (−), 134.5 (−), 136.4 (+), 138.8 (+), 191.6 (−), 194.3 (+); GC−MS (EI) obsd 194, 152, 119, 91. Anal. Calcd for $C_{10}H_{10}O_2S$, C, 61.83; H, 5.19; S, 16.51. Found: C, 61.72; H, 5.25; S, 16.64.

General Procedure for Synthesis of Porphyrins 17−22 and 24−26. The acetal (**4**, **5**, **6**, or **7**) (0.730 mmol) was dissolved in CH_2Cl_2 (1 mL), and trifluoroacetic acid (2 mL) was added. The mixture was stirred at room temperature overnight. After evaporation of the reaction mixture to dryness, the residue was redissolved in $CHCl_3$ (40 mL). Alternatively, aldehyde **8** or 4-(methylthio)benzaldehyde (0.730 mmol) was added to $CHCl_3$ (40 mL). Next, samples of the other aldehyde (2.20 mmol), pyrrole (0.200 mL, 2.92 mmol), and $BF_3{\cdot}OEt_2$ (0.090 mL, 0.71 mmol) were added. The reaction mixture was stirred at room temperature for 90 min. Then DDQ (500 mg, 2.20 mmol) was added, and the reaction mixture was gently refluxed for 1 h. After cooling, the reaction mixture was passed over a short silica column (CH_2Cl_2), affording porphyrins usually free from dark pigments and quinone species. Further purification details are described for each case as follows.

5,10,15-Trimesityl-20-[4-[*S*-(*N*-ethylcarbamoyl)thio]phenyl]porphyrin (17). The mixture of porphyrins was loaded onto a silica column (toluene). The title porphyrin comprised the second purple band, affording 72 mg (12%): ^{1}H NMR δ −2.47 (s, 2H), 1.32 (t, 3H, J = 7.2 Hz), 1.94 (s, 18H), 2.69 (s, 9H), 3.4−3.6 (m, 2H), 5.65 (br s, 1H), 7.35 (s, 6H), 8.00, 8.33 (AA′BB′, 4H), 8.72 (s, 4H), 8.78 (d, 2H, J = 4.2 Hz), 8.87 (d, 2H, J = 4.2 Hz); LD-MS obsd 844.6 [M$^+$], 773.1 [M$^+$ − CONHEt]; FAB-MS obsd 843.4019, calcd exact mass 843.3971 ($C_{56}H_{53}N_5OS$); λ_{abs} (CH_2Cl_2) 419, 515, 548, 591 nm.

5,10,15-Trimesityl-20-[4-[*S*-(2,4-dinitrophenyl)thio]phenyl]porphyrin (18). The mixture of porphyrins was purified by preparative centrifugal chromatography (silica, toluene/hexanes, 1:2). The title porphyrin comprised the second purple band, affording 70 mg (10%): ^{1}H NMR δ −2.44 (s, 2H), 1.95 (s, 18H), 2.71 (s, 9H), 7.30 (d, 1H, J = 8.1 Hz), 7.37 (s, 6H), 7.60 (d, 1H, J = 8.7 Hz), 8.00, 8.49 (AA′BB′, 4H), 8.75 (s, 4H), 8.8−9.0 (m, 4H), 9.30 (d, 1H, J = 2.1 Hz); LD-MS obsd 938.0; FAB-MS obsd 938.3632, calcd exact mass 938.3614 ($C_{59}H_{50}N_6O_4S$); λ_{abs} (CH_2Cl_2) 419, 515, 549, 591, 646 nm.

5,10,15-Trimesityl-20-[4-[*S*-(9-anthrylmethyl)thio]phenyl]porphyrin (19). The mixture was chromatographed on an alumina column (toluene/hexanes, 1:4). The resulting mixture of porphyrins was purified by preparative centrifugal chromatography (silica, toluene/hexanes, 1:3). The title porphyrin comprised the second purple band, affording 28 mg (4.0%): ^{1}H NMR δ −2.51 (s, 2H), 1.90 (s, 18H), 2.66 (s, 9H), 5.43 (s, 2H), 7.1−7.8 (m, 5H), 7.31 (s, 6H), 7.79, 8.52 (AA′BB′, 4H), 8.0−8.2 (m, 4H), 8.68 (s, 4H), 8.75 (d, 2H, J = 4.5 Hz), 8.80 (d, 2H, J = 4.5 Hz); LD-MS obsd 964.0, 787.4 [M$^+$ − $C_{14}H_8$], 773.1 [M$^+$ − $C_{15}H_{10}$]; FAB-MS obsd 962.4368, calcd exact mass 962.4382 ($C_{68}H_{58}N_4S$); λ_{abs} (CH_2Cl_2) 420, 515, 549, 593, 648 nm.

5,10,15-Trimesityl-20-[4-(*S*-pivaloylthio)phenyl]porphyrin (20). The mixture was chromatographed on a silica column (toluene/hexanes, 1:1). The title porphyrin comprised the second purple band, affording 68 mg (11%): ^{1}H NMR δ −2.49 (s, 2H), 1.52 (s, 9H), 1.92 (s, 18H), 2.68 (s, 9H), 7.35 (s, 6H), 7.83, 8.30 (AA′BB′, 4H), 8.70 (s, 4H), 8.75 (d, 2H, J = 5.4 Hz), 8.88 (d, 2H, J = 5.4 Hz); LD-MS obsd 858.6, 831.5 [M$^+$ − C_2H_6], 774.2 [M$^+$ − COC(CH$_3$)$_3$]; FAB-MS obsd 856.4186, calcd exact mass 856.4175 ($C_{58}H_{56}N_4OS$); λ_{abs} (CH_2Cl_2) 419, 515, 548, 591, 646 nm.

5,10,15-Trimesityl-20-[4-(methylthio)phenyl]porphyrin (21). The mixture was chromatographed on one silica column (toluene/hexanes, 1:1) and then on a second silica column (toluene/hexanes, 1:4). The title porphyrin comprised the second purple band, affording 57 mg (10%): ^{1}H NMR δ −2.49 (s, 2H), 1.92 (s, 18H), 2.68 (s, 9H), 2.79 (s, 3H), 7.33 (s, 6H), 7.67, 8.18 (AA′BB′, 4H), 8.70 (s, 4H), 8.74 (d, 2H, J = 5.1 Hz), 8.87 (d, 2H, J = 5.1 Hz); LD-MS obsd 786.9; FAB-MS obsd 786.3790, calcd exact mass 786.3756 ($C_{54}H_{50}N_4S$); λ_{abs} (CH_2Cl_2) 420, 515, 550, 592, 648 nm.

5,10,15-Trimesityl-20-[4-(*S*-acetylthio)phenyl]porphyrin (22). The mixture was chromatographed on a silica column (toluene/hexanes, 1:1, then toluene). The title porphyrin comprised the second purple band, affording 62 mg (10.5%): ^{1}H NMR δ −2.46 (s, 2H), 1.94 (s, 18H), 2.66 (s, 3H), 2.70 (s, 9H), 7.35 (s, 6H), 7.88, 8.35 (AA′BB′, 4H), 8.73 (s, 4H), 8.79 (d, 2H, J = 4.2 Hz), 8.89 (d, 2H, J = 4.2 Hz); LD-MS obsd 815.7, 830.9 [M$^+$ + 15]; 787.7 [M$^+$ − CH$_3$CO + 15], 773.7 [M$^+$ − CH$_3$CO]; FAB-MS obsd 814.3694, calcd exact mass 814.3705 ($C_{55}H_{50}N_4OS$); λ_{abs} (CH_2Cl_2) 419, 515, 548, 591, 647 nm.

5,10,15-Tris(2,4,6-trimethoxyphenyl)-20-[4-[*S*-(*N*-ethylcarbamoyl)thio]phenyl]porphyrin (24). Purification was performed by preparative centrifugal chromatography (silica, CH_2Cl_2/methanol, 98:2). The title compound was obtained as a 1:1 mixture with 5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphyrin. The presence of the title compound was confirmed by mass spectrometry (LD-MS $C_{56}H_{53}N_5O_{10}S$ calcd average mass 987.4, obsd 988.6). This mixture was not purified further but was used in the metalation reaction to prepare **Zn-24**.

5,10,15-Tris(2,3,4,5,6-pentafluorophenyl)-20-[4-[*S*-(*N*-ethylcarbamoyl)thio]phenyl]porphyrin (25). The mixture of porphyrins was chromatographed on a silica column (hexanes/CH_2Cl_2, 2:1). The title porphyrin comprised the second purple band, affording 72 mg (10%): ^{1}H NMR δ −2.74 (s, 2H), 1.32 (t, 3H, J = 7.2 Hz), 3.5−3.6 (m, 2H), 5.67 (br s, 1H), 8.00, 8.32 (AA′BB′, 4H), 8.94 (d, 2H, J = 5.1 Hz), 9.02 (s, 4H), 9.09 (d, 2H, J = 4.2 Hz); LD-MS obsd 989.9, 918.7 [M$^+$ − CONHEt]; FAB-MS obsd 987.1136, calcd exact mass 987.1149 ($C_{47}H_{20}F_{15}N_5OS$); λ_{abs} (CH_2Cl_2) 415, 509, 540, 584, 638 nm.

5,10,15-Tri-*n*-pentyl-20-[4-[*S*-(*N*-ethylcarbamoyl)thio]phenyl]porphyrin (26). The free base was purified by preparative centrifugal chromatography (silica/CH_2Cl_2/hexanes, 5:1) followed by column chromatography (silica/CH_2Cl_2/toluene, 4:1). The title porphyrin comprised the second purple band, affording 9 mg (4%): ^{1}H NMR δ −2.62 (s, 2H), 1.00−1.10 (m, 9H), 1.30−1.70 (m, 9H), 1.75−1.90 (m, 6H), 2.45−2.70 (m, 6H), 3.50−3.62 (m, 4H), 4.90−5.10 (m, 6H), 5.63 (br t, 1H, J = 5.1 Hz), 7.98, 8.26 (AA′BB′, 4H), 8.85 (d, 2H, J = 4.2 Hz), 9.43 (d, 2H, J = 5.1 Hz); 9.52−9.62 (m, 4H); LD-MS obsd 700.7; FAB-MS obsd 699.3996, calcd exact mass 699.3971 ($C_{44}H_{53}N_5OS$); λ_{abs} (CH_2Cl_2) 419, 519, 554, 598, 656 nm.

General Procedure for Zinc Insertion. The porphyrin (0.040 mmol) was dissolved in CH_2Cl_2 (15 mL), and a solution of $Zn(OAc)_2{\cdot}2H_2O$ (880 mg, 4.00 mmol) in methanol (15 mL) was added. The reaction mixture was stirred overnight at room temperature. After metalation was complete (TLC, fluorescence excitation spectroscopy), the reaction mixture was washed with water and 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated to a purple solid. Purification was achieved by chromatography on silica.

Zinc(II)−5,10,15-Trimesityl-20-[4-[*S*-(*N*-ethylcarbamoyl)thio]phenyl]porphyrin (Zn-17). Column chromatography (silica, CH_2Cl_2) afforded 29 mg (75%): ^{1}H NMR δ 1.30 (t, 3H, J = 7.5 Hz), 1.87 (s, 18H), 2.66 (s, 9H), 3.4−3.6 (m, 2H), 5.61 (br s, 1H), 7.31 (s, 6H), 7.93, 8.30 (AA′BB′, 4H), 8.74 (s, 4H), 8.80 (d, 2H, J = 5.1 Hz), 8.88 (d, 2H, J = 4.2 Hz); LD-MS obsd 906.7, 835.7 [M$^+$ − CONHEt]; FAB-MS obsd 905.3098, calcd exact mass 905.3106 ($C_{56}H_{51}N_5OSZn$); λ_{abs} (CH_2Cl_2) 421, 549 nm.

Zinc(II)−5,10,15-Trimesityl-20-[4-[*S*-(2,4-dinitrophenyl)thio]phenyl]porphyrin (Zn-18). Column chromatography

(silica, toluene/hexanes) afforded 34 mg (85%): ^{1}H NMR δ 1.87 (s, 18H), 2.64 (s, 9H), 7.26 (d, 1H, J = 9.0 Hz), 7.29 (s, 6H), 7.54 (d, 1H, J = 9.0 Hz), 7.99, 8.44 (AA′BB′, 4H), 8.75 (s, 4H), 8.86 (AB, 4H, J = 4.5 Hz), 9.23 (d, 1H, J = 3.0 Hz); LD-MS obsd 1000.3; FAB-MS obsd 1000.2726, calcd exact mass 1000.2749 ($C_{59}H_{48}N_6O_4SZn$); λ_{abs} (CH_2Cl_2) 422, 550 nm.

Zinc(II)−5,10,15-Trimesityl-20-[4-[*S*-(9-anthrylmethyl)-thio]phenyl]porphyrin (Zn-19). The product was purified by preparative centrifugal chromatography (silica, hexanes/CH_2Cl_2) 31 mg (74%): ^{1}H NMR δ 1.85 (s, 9H), 1.88 (s, 9H), 2.65 (s, 9H), 5.36 (s, 2H), 7.1−8.5 (m, 19H), 8.72 (s, 2H), 8.73 (s, 2H), 8.8−9.0 (m, 4H); LD-MS obsd 1027.3, 850.0 [$M^+ - C_{14}H_8$], 834.9 [$M^+ - C_{15}H_{10}$]; FAB-MS obsd 1024.3529, calcd exact mass 1024.3517 ($C_{68}H_{56}N_4SZn$); λ_{abs} (CH_2Cl_2) 421, 550 nm.

Zinc(II)−5,10,15-Trimesityl-20-[4-(*S*-pivaloylthio)phenyl]porphyrin (Zn-20). The product was purified on a silica column (toluene/hexanes, 1:1), affording 31 mg (85%): ^{1}H NMR δ 1.50 (s, 9H), 1.87 (s, 18H), 2.65 (s, 9H), 7.31 (s, 6H), 7.79, 8.29 (AA′BB′, 4H), 8.74 (s, 4H), 8.79 (d, 2H, J = 4.2 Hz), 8.91 (d, 2H, J = 4.2 Hz); LD-MS obsd 919.5, 891.4 [$M^+ - C_2H_6$], 835.3 [$M^+ - COC(CH_3)_3$]; FAB-MS obsd 918.3332, calcd exact mass 918.3310 ($C_{58}H_{54}N_4OSZn$); λ_{abs} (CH_2Cl_2) 422, 549 nm.

Zinc(II)−5,10,15-Trimesityl-20-[4-(methylthio)phenyl]-porphyrin (Zn-21). The mixture was chromatographed on a silica column (toluene/hexanes, 1:1). The resulting mixture was next chromatographed on a silica column (toluene/hexanes, 1:4). The title porphyrin comprised the second purple band, affording 31 mg (90%): ^{1}H NMR δ 1.84 (s, 18H), 2.63 (s, 9H), 2.74 (s, 3H),7.26 (s, 6H), 7.59, 8.13 (AA′BB′, 2H), 8.70 (s, 4H), 8.75 (d, 2H, J = 5.1 Hz), 8.87 (d, 2H, J = 5.1 Hz); LD-MS obsd 851.5; FAB-MS obsd 848.2913, calcd exact mass 848.2891 ($C_{54}H_{48}N_4SZn$); λ_{abs} (CH_2Cl_2) 421, 550 nm.

Zinc(II)−5,10,15-Trimesityl-20-[4-(*S*-acetylthio)phenyl]-porphyrin (Zn-22). Method I. (From **22** by general zinc insertion procedure). Purification by chromatography (silica, toluene/CH_2Cl_2), yield 82%. **Method II.** Porphyrin **Zn-17** (9.0 mg, 0.010 mmol) was dissolved in CH_2Cl_2 (20 mL), and the solution was carefully flushed with argon. Next, a solution of sodium methoxide [freshly prepared from sodium (23 mg, 1.0 mmol) and methanol (10 mL) under argon] was added. The reaction mixture was stirred under argon at room temperature for 1 h. Then, acetyl chloride (1 mmol, 0.7 mL) was added, and the mixture was evaporated to dryness. The mixture of porphyrins was dissolved in CH_2Cl_2 and chromatographed (silica, hexanes/CH_2Cl_2) affording 6.3 mg (72%): ^{1}H NMR δ 1.85 (s, 18H), 2.63 (s, 9H), 2.61 (s, 3H), 7.28 (s, 6H), 7.46, 8.07 (AA′BB′, 4H), 8.70 (s, 4H), 8.74 (d, 2H, J = 5.1 Hz), 8.83 (d, 2H, J = 5.1 Hz); LD-MS obsd 874.6; FAB-MS obsd 878.2983, calcd exact mass 878.2997 ($C_{55}H_{50}N_4OSZn$); λ_{abs} (CH_2Cl_2) 421, 550 nm.

Zinc(II)−5,10,15-Trimesityl-20-[4-mercaptophenyl]porphyrin (Zn-23). A sample of **Zn-17** (9.0 mg, 0.010 mmol) was dissolved in CH_2Cl_2 (20 mL) and the solution was carefully flushed with argon. Next a solution of sodium methoxide [freshly prepared from sodium (23 mg, 1 mmol) and methanol (10 mL) under argon] was added. The reaction mixture was stirred at room temperature for 1 h, HCl (0.2 mL, 5 M solution) was added, and the mixture was evaporated to dryness. The mixture of porphyrins was dissolved in CH_2Cl_2 and chromatographed (silica, hexanes/CH_2Cl_2), affording 4.3 mg (51%): ^{1}H NMR δ 1.89 (s, 18H), 2.66 (s, 9H), 7.31 (s, 6H), 7.64, 8.22 (AA′BB′, 2H), 8.76 (s, 4H), 8.8−9.0 (m, 4H); LD-MS obsd 834.0; FAB-MS obsd 834.2071, calcd exact mass 834.2735 ($C_{53}H_{46}N_4SZn$); λ_{abs} (CH_2Cl_2) 421, 550 nm.

Zinc(II)−5,10,15-Tris(2,4,6-trimethoxyphenyl)-20-[4-[*S*-(*N*-ethylcarbamoyl)thio]phenyl]porphyrin (Zn-24). 30.0 mg of a mixture of the desired free base A_3B-porphyrin and the corresponding A_4-porphyrin was metalated according to the general procedure. The desired chelate was purified by preparative centrifugal chromatography (silica, CH_2Cl_2/methanol, 99:1), affording 10.0 mg (1.3% from acetal **4**): ^{1}H NMR δ 1.27 (t, 3H, J = 7.2 Hz), 3.4−3.6 (m, 2H), 3.49 (s, 18H), 4.09 (s, 9H), 5.57 (br t, 1H, J = 5.1 Hz), 6.57 (s, 6H), 7.89, 8.26 (AA′BB′, 4H), 8.81 (d, 2H, J = 4.5 Hz), 8.86 (d, 2H, J = 4.5 Hz), 8.84 (s, 4H); LD-MS obsd 1052.7, 981.5 [M^+ − CONHEt]; FAB-MS obsd 1049.2666, calcd exact mass 1049.2648 ($C_{56}H_{51}N_5O_{10}SZn$); λ_{abs} (CH_2Cl_2) 423, 549 nm.

Zinc(II)−5,10,15-Tris(2,3,4,5,6-pentafluorophenyl)-20-[4-mercaptophenyl]porphyrin (Zn-27). Refluxing a mixture of porphyrin **25** and $Zn(OAc)_2$·$2H_2O$ for 8 h followed by purification on silica (CH_2Cl_2) afforded 25 mg (63% yield): ^{1}H NMR δ 3.79 (s, 1H), 7.67, 8.09 (AA′BB′, 4H), 8.93 (d, 2H, J = 4.2 Hz), 9.00 (s, 4H), 9.09 (d, 2H, J = 4.2 Hz); LD-MS obsd 975.4; FAB-MS obsd 977.9925, calcd exact mass 977.9913 ($C_{44}H_{13}F_{15}N_4SZn$); λ_{abs} (CH_2Cl_2) 416, 545 nm.

Zinc(II)−5,10,15-Tri-*n*-pentyl-20-[4-mercaptophenyl]-porphyrin (Zn-28). The product was purified by column chromatography (silica/CH_2Cl_2) followed by preparative centrifugal chromatography (silica, hexanes/CH_2Cl_2, 1:9), affording 12 mg (44%): ^{1}H NMR δ 0.80−1.40 (m, 12H), 1.50−1.70 (m, 6H), 1.75−1.95 (m, 6H), 2.40−2.60 (m, 6H), 4.70−4.90 (m, 6H), 8.17, 8.28 (AA′BB′, 4H), 8.95 (d, 2H, J = 5.1 Hz), 9.35−9.48 (d, 6H); LD-MS obsd 690.4, 633.1 [$M^+ - C_4H_9$]; FAB-MS obsd 690.2706, calcd exact mass 690.2735 ($C_{41}H_{46}N_4SZn$); λ_{abs} (CH_2Cl_2) 419, 554 nm.

5,10,15,20-Tetrakis[3-(thiocyanatomethyl)phenyl]porphyrin (29). A solution of **11** (513 mg, 2.9 mmol) and pyrrole (0.20 mL, 2.9 mmol) in $CHCl_3$ (300 mL) was purged with argon for 30 min. Under stirring at room temperature, BF_3·OEt_2 (12 μL, 0.1 mmol) and TFA (180 μL, 2.3 mmol) were added in the dark. Soon the solution turned yellow and later to dark red. After 2 h, additional BF_3·OEt_2 (90 μL, 0.7 mmol) was added. After a further 2 h, triethylamine (500 μL, 3.6 mmol) and *o*-tetrachlorobenzoquinone (583 mg, 2.4 mmol) were added, and the mixture was refluxed for 1 h. The mixture was cooled to room temperature, and the solvents were removed under reduced pressure. Column chromatography over flash silica gel (ethyl ether/hexanes, 3:1) gave 119 mg (18% yield) of a dark purple solid: IR (neat) $\tilde{\nu}$ 2953, 2917, 2846, 2152; ^{1}H NMR δ −2.84 (s, 2H), 4.44 (s, 8H), 7.76−7.85 (m, 8H), 8.18−8.25 (m, 8H), 8.88 (s, 8H); LD-MS obsd 898.0 [M^+], 871.0 [$M^+ - CN$], 839.9 [$M^+ - SCN$], 781.9 [$M^+ - 2\ SCN$], 724.9 [$M^+ - 3\ SCN$], 666.7 [$M^+ - 4\ SCN$]; FAB-MS obsd 898.1797, calcd exact mass 898.1789 ($C_{52}H_{34}N_8S_4$); λ_{abs} (toluene) 420, 514, 549, 590, 646 nm.

Zinc(II)−5,10,15,20-Tetrakis[3-(thiocyanatomethyl)-phenyl]porphyrin (Zn-29). To a solution of **27** (84 mg, 93 μmol) in $CHCl_3$ (50 mL) was added 5 mL of a methanolic solution of $Zn(OAc)_2$·$2H_2O$ (250 mg, 1.1 mmol) with stirring at room temperature in the dark. After completion of the metalation, the mixture was washed with 10% $NaHCO_3$ solution (20 mL) and water (20 mL), dried (Na_2SO_4), and filtered. The solvents were removed under reduced pressure, affording 71 mg (79% yield) of a dark purple solid. Recrystallization (CH_2Cl_2/methanol) gave dark purple crystals: IR (neat) $\tilde{\nu}$ 2995, 2880, 2153, 1601; ^{1}H NMR δ 4.44 (s, 8H), 7.77−7.83 (m, 8H), 8.20−8.25 (m, 8H), 8.97 (s, 8H); LD-MS obsd 961.1 [M^+], 903.0 [$M^+ - SCN$], 845.0 [$M^+ - 2\ SCN$], 786.9 [$M^+ - 3\ SCN$], 727.9 [$M^+ - 4\ SCN$]; FAB-MS obsd 960.0959, calcd exact mass 960.0924 ($C_{52}H_{32}N_8S_4Zn$); λ_{abs} (toluene) 422, 550, 589 nm; λ_{em} (toluene) 603, 652 nm.

5,10,15,20-Tetrakis[3-(*S*-acetylthiomethyl)phenyl]porphyrin (30). Method I. A solution of 5,10,15,20-tetrakis[3-(bromomethyl)phenyl)porphyrin[13,40] (102 μmol) and potassium thioacetate (60 mg, 525 μmol) in THF (20 mL) was refluxed in the dark. After 5 h, the mixture was cooled to room temperature. Water (30 mL) was added, and the phases were separated. The organic phase was washed with 5% $NaHCO_3$ solution (40 mL) and dried (Na_2SO_4). Column chromatography over flash silica gel with THF afforded a purple wax, which was purified by refluxing in hexanes. The mixture was filtered, and the residue was dissolved in CH_2Cl_2. The solvent was removed under reduced pressure, affording 63 mg (63% yield) of a purple solid. **Method II.** To a solution of aldehyde **12** (525 mg, 3.0 mmol), pyrrole (206 μL, 3.0 mmol), and TFA (185 μL, 2.4 mmol) in CH_2Cl_2 (300 mL) was added BF_3·OEt_2 (13 μL, 0.1 mmol) with stirring at room temperature in the dark under argon. The solution turned yellow and later dark red. After 3 h, DDQ (505 mg, 2.2 mmol) was added, and the mixture was

refluxed. After 1.5 h, the mixture was cooled to room temperature, and the solvents were removed under reduced pressure. Column chromatography over flash silica gel (ethyl ether/hexanes, 1:1) was performed twice, affording 226 mg (32% yield) of a purple solid: IR (neat) $\tilde{\nu}$ 3423, 3318, 2963, 2926, 1690, 1600; ^{1}H NMR δ −2.83 (s, 2H), 2.40 (s, 12H), 4.41 (s, 8H), 7.65−7.75 (m, 8H), 8.06−8.17 (m, 8H), 8.84 (s, 8H); LD-MS obsd 982.4 [M^+ + 15], 967.4 [M^+], 925.3 [$M^+ - COCH_3$], 892.2 [$M^+ - SCOCH_3$], 850.0 [$M^+ - SCOCH_3 - COCH_3$], 817.2 [$M^+ - 2\ SCOCH_3$], 775.5 [$M^+ - 2\ SCOCH_3 - COCH_3$]; FAB-MS obsd 966.2413, calcd exact mass 966.2402 ($C_{56}H_{46}N_4O_4S_4$); λ_{abs} (toluene) 421, 515, 550, 591, 648 nm.

Zinc(II)−5,10,15,20-Tetrakis[3-(*S*-acetylthiomethyl)-phenyl]porphyrin (Zn-30). A solution of **30** (16.2 mg, 16.7 μmol) in $CHCl_3$ (20 mL) was treated with 5 mL of a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (80.0 mg, 365 μmol) with stirring at room temperature in the dark. After 2 h, the metalation was completed, and water (40 mL) was added. The phases were separated, and the organic layer was washed three times with 5% $NaHCO_3$ and dried (Na_2SO_4). The solvents were removed under reduced pressure. Column chromatography over flash silica gel (CH_2Cl_2/hexanes, 4:1) gave the title compound as a purple solid in quantitative yield: IR (neat) $\tilde{\nu}$ 2922, 2849, 1690, 1600; ^{1}H NMR: δ 2.30 (s, 12H), 4.31 (s, 8H), 7.62−7.69 (m, 8H), 8.05−8.13 (m, 8H), 8.92 (s, 8H); LD-MS, obsd 1043.6 [M^+ + 15], 1028.8 [M^+], 986.6 [$M^+ - COCH_3$], 954.7 [$M^+ - SCOCH_3$], 911.3 [$M^+ - SCOCH_3 - COCH_3$], 880.4 [$M^+ - 2\ SCOCH_3$], 838.8 [$M^+ - 2\ SCOCH_3 - COCH_3$], 805.3 [$M^+ - 3\ SCOCH_3$]; ($C_{56}H_{44}N_4O_4S_4Zn$), FAB-MS obsd 1028.1560, calcd exact mass 1028.1537 ($C_{56}H_{44}N_4O_4S_4Zn$); λ_{abs} (toluene) 424, 550, 589 nm; λ_{em} (toluene) 597, 647 nm.

Cobalt(II)−5,10,15,20-Tetrakis[3-(*S*-acetylthiomethyl)-phenyl]porphyrin (Co-30). A solution of **30** (14.2 mg, 14.7 μmol) in $CHCl_3$ (20 mL) was treated with 5 mL of a methanolic solution of $Co(OAc)_2 \cdot 4H_2O$ (60.0 mg, 339 μmol) with stirring at room temperature in the dark. After 5 h, additional $Co(OAc)_2 \cdot 4H_2O$ (261.0 mg, 1.5 mmol) was added, and stirring was continued. After 20 h, the metalation was completed and the mixture was worked up in the general way. Column chromatography over flash silica gel (CH_2Cl_2/hexanes, 5:1) gave the title compound as an orange-purple solid in quantitative yield: IR (neat) $\tilde{\nu}$ 3037, 2955, 2924, 1693, 1601; LD-MS obsd 1038.4 [M^+ + 15], 1023.4 [M^+], 980.3 [$M^+ - COCH_3$], 948.3 [$M^+ - SCOCH_3$], 875.2 [$M^+ - 2\ SCOCH_3$]; FAB-MS obsd 1023.1611, calcd exact mass 1023.1577 ($C_{56}H_{44}N_4O_4S_4Co$); λ_{abs} (toluene) 414, 529 nm.

Copper(II)−5,10,15,20-Tetrakis[3-(*S*-acetylthiomethyl)-phenyl]porphyrin (Cu-30). A solution of **30** (14.0 mg, 14.5 μmol) in $CHCl_3$ (20 mL) was treated with 5 mL of a methanolic solution of $Cu(OAc)_2 \cdot H_2O$ (60.0 mg, 301 μmol) with stirring at room temperature in the dark. After 2.5 h, the metalation was completed, and the mixture was worked up in the general way. Column chromatography over flash silica gel (CH_2Cl_2/hexanes, 5:1) gave 13.2 mg (89%) of the title compound as an orange-purple solid: IR (neat) $\tilde{\nu}$ 2922, 2851, 1691, 1600; LD-MS obsd 1043.3 [M^+ + 15], 1028.3 [M^+], 984.3 [$M^+ - COCH_3$], 953.2 [$M^+ - SCOCH_3$], 911.0 [$M^+ - SCOCH_3 - COCH_3$], 878.1 [$M^+ - 2\ SCOCH_3$]; FAB-MS obsd 1027.1570, calcd exact mass 1027.1541 ($C_{56}H_{44}N_4O_4S_4Cu$), λ_{abs} (toluene) 419, 541 nm.

Silver(II)−5,10,15,20-Tetrakis[3-(*S*-acetylthiomethyl)-phenyl]porphyrin (Ag-30). A solution of **30** (13.1 mg, 13.5 μmol) in $CHCl_3$ (20 mL) was treated with 5 mL of a methanolic solution of $AgNO_3$ (50.0 mg, 294 μmol) with stirring at room temperature in the dark. In 3 h a brown precipitation formed and the solution turned green; upon adding triethylamine (0.5 mL) the mixture turned back to red. After an additional 2 h, the metalation was completed and the mixture was worked up in the general way. Column chromatography over flash silica gel (CH_2Cl_2/hexanes, 4:1) gave 4.8 mg (33%) of the title compound as a purple solid: IR (neat) $\tilde{\nu}$ 2921, 2850, 1684; LD-MS obsd 1086.5 [M^+ + 15], 1071.5 [M^+], 1028.4 [$M^+ - COCH_3$], 996.4 [$M^+ - SCOCH_3$], 954.3 [$M^+ - SCOCH_3 - COCH_3$], 921.3 [$M^+ - 2\ SCOCH_3$]; FAB-MS obsd 1071.1281, calcd exact mass 1071.1296 ($C_{56}H_{44}N_4O_4S_4Ag$); λ_{abs} (toluene) 429, 543 nm.

10,20-Diphenyl-5,15-bis[3-(thiocyanatomethyl)phenyl]-porphyrin (31). A mixture of **11** (316 mg, 1.8 mmol), 5-phenyldipyrromethane (396 mg, 1.8 mmol), and NH_4Cl (1.07 g, 20.0 mmol) in acetonitrile (200 mL) was purged with argon for 30 min. Then $BF_3 \cdot OEt_2$ (23 μL, 0.18 mmol) was added with stirring at room temperature in the dark. Soon the solution turned yellow and later dark red. After 6.5 h, DDQ (607 mg, 2.7 mmol) was added. After an additional 1 h, the reaction was quenched with triethylamine (0.5 mL, 3.6 mmol). The solvents were removed under reduced pressure. Purification was done by column chromatography over two flash silica gel columns with different solvent mixtures: (column 1) ethyl ether/hexanes (3:1) and (column 2) CH_2Cl_2/hexanes (gradient, start: 1:1). Two fractions of dark purple solids were obtained. I: 12 mg 10,15,20-triphenyl-5-[3-(thiocyanatomethyl)phenyl]-porphyrin (2% yield). II: 44 mg of the title compound (7% yield): IR (neat) $\tilde{\nu}$ 2921, 2850, 2154, 1597; ^{1}H NMR δ −2.81 (s, 2H), 4.57 (s, 4H), 7.71−7.83 (m, 11H), 8.17−8.25 (m, 8H), 8.84 (d, 4H, ^3J = 5.1 Hz), 8.88 (d, 4H); LD-MS obsd 757.4 [M^+], 699.2 [$M^+ - SCN$], 641.0 [$M^+ - 2\ SCN$]; FAB-MS obsd 756.2172, calcd exact mass 756.2130 ($C_{48}H_{32}N_6S_2$); λ_{abs} (toluene) 420, 514, 549, 590, 647 nm.

Zinc(II)−10,20-Diphenyl-5,15-bis[3-(thiocyanatomethyl)phenyl]porphyrin (Zn-31). A solution of **28** (38 mg, 50.2 μmol) in CH_2Cl_2 (30 mL) was treated with 5 mL of a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (140 mg, 0.64 mmol) with stirring at room temperature in the dark. After completion of the metalation, water (20 mL) was added, the phases were separated and the organic layer was washed with 5% $NaHCO_3$ solution (20 mL) and water (20 mL), dried (Na_2SO_4), and filtered. The solvents were removed under reduced pressure. Column chromatography over flash silica gel (CH_2Cl_2/hexanes, 5:1) gave 22 mg (53% yield) of a dark purple solid: IR (neat) $\tilde{\nu}$ 3049, 2924, 2853, 2154, 1598; ^{1}H NMR δ 4.44 (s, 4H), 7.70−7.90 (m, 11H), 8.16−8.28 (m, 8H), 8.93 (d, 4H, ^3J = 4.2 Hz), 8.98 (d, 4H); LD-MS obsd 819.6 [M^+], 792.3 [$M^+ - CN$], 761.5 [$M^+ - SCN$], 703.3 [$M^+ - 2\ SCN$], 626.0 [$M^+ - 2\ SCN - C_6H_5$], 613.5 [$M^+ - 2\ SCN - C_7H_7$]; FAB-MS obsd 818.1275, calcd exact mass 818.1265 ($C_{48}H_{30}N_6S_2Zn$); λ_{abs} (toluene) 424, 550, 590 nm; λ_{em} (toluene) 599, 647 nm.

5,15-Dimesityl-10-[4-iodophenyl]-20-[4-(*S*-acetylthio)-phenyl]porphyrin (32). Acetonitrile (500 mL) was degassed with a stream of Ar for 10 min. Freshly ground NH_4Cl (2.68 g, 50 mmol) was added, and the flask was placed in an ice-bath and cooled under Ar. Samples of 5-mesityldipyrromethane (1320 mg, 5.0 mmol), 4-iodobenzaldehyde (575 mg, 2.5 mmol), and aldehyde **8** (450 mg, 2.5 mmol) were added, followed by $BF_3 \cdot OEt_2$ (0.63 mL, 0.5 mmol), and the mixture was stirred at 0 °C under Ar. After 6 h, DDQ (1.70 g, 7.5 mmol) was added. The ice bath was removed, and the mixture was stirred at room temperature overnight. Removal of the solvents gave a black solid that was filtered through a pad of silica and eluted with toluene. Next, the mixture of porphyrins was chromatographed on a silica column (toluene/hexanes 1:1, then toluene). The title porphyrin comprised the second purple band, affording 109 mg (4.9%): ^{1}H NMR δ −2.65 (s, 2H), 1.84 (s, 12H), 2.61 (s, 3H), 2.64 (s, 6H), 7.29 (s, 4H), 7.81, 8.08 (AA′BB′, 4H), 7.96, 8.27 (AA′BB′, 4H), 8.7−8.9 (m, 8H); LD-MS obsd 902.3, 917.4 [M^+ + 15]; 860.1 [$M^+ - CH_3CO$]; 775.7 [$M^+ - I$]; 734.5 [$M^+ - CH_3CO - I$], FAB-MS obsd 898.2186, calcd exact mass 898.2202 ($C_{52}H_{43}IN_4OS$); λ_{abs} (CH_2Cl_2) 419, 515, 549, 590, 646 nm.

10,20-Bis[3-(*S*-acetylthiomethyl)phenyl]-5,15-bis-(3-iodophenyl)porphyrin (33). A mixture of aldehyde **12** (1.943 g, 10.0 mmol), 5-(3-iodophenyl)dipyrromethane (3.483 mg, 10.0 mmol), and NH_4Cl (5.349 g, 100.0 mmol) in acetonitrile (1 L) was purged with argon for 30 min and stirred in an ice bath in the dark. Then $BF_3 \cdot OEt_2$ (127 μL, 1.0 mmol) was added. Soon the reaction mixture turned yellow and later dark red. After 4.5 h, DDQ (3.406 g, 15.0 mmol) was added, and the ice-bath was removed. After an additional hour, the reaction was filtered through a pad of alumina and eluted with CH_2Cl_2. The solvents were removed under reduced pressure, and the black solid was dissolved in toluene (200 mL). DDQ (2.271 g, 10.0 mmol) was added, and the mixture was refluxed for 1 h. The

mixture was cooled to room temperature, filtered through a pad of alumina, and eluted with CH_2Cl_2. Purification by column chromatography (silica, CH_2Cl_2/hexanes, 2:1) afforded two fractions of dark brown purple solids, I, 112 mg of 10,20-bis[3-(*S*-acetylthiomethyl)phenyl]-5,15-bis(3-iodophenyl)porphyrin (2% yield); II, 153 mg of the title compound (3% yield): IR (neat) $\tilde{\nu}$ 3316, 2923, 2852, 1691, 1583, 1554; ^{1}H NMR δ −2.87 (s, 2H), 2.41 (s, 6H), 4.42 (s, 4H), 7.45−7.53 (m, 2H), 7.66−7.76 (m, 4H), 8.07−8.22 (m, 8H), 8.59 (s, 2H), 8.82−8.89 (m, 8H); LD-MS obsd 1057.4 [M^+ + 15], 1042.3 [M^+], 999.2 [$M^+ - COCH_3$], 967.3 [$M^+ - SCOCH_3$], 916.2 [M^+ − I], 892.0 [$M^+ - 2\ COCH_3$], 874.1 [$M^+ - I - COCH_3$], 841.1 [$M^+ - I - SCOCH_3$]; FAB-MS obsd 1042.0355, calcd exact mass 1042.0369 ($C_{50}H_{36}I_2N_4O_2S_2$); λ_{abs} (toluene) 421, 515, 550, 591, 647 nm.

10,20-Bis[3-(thiocyanatomethyl)phenyl]-5,15-bis-(3-iodophenyl)porphyrin (34). A mixture of **11** (1.056 g, 6.0 mmol), 5-(3-iodophenyl)dipyrromethane (2.075 mg, 6.0 mmol), and NH_4Cl (3.209 g, 60.0 mmol) in acetonitrile (600 mL) was purged with argon for 30 min. Then $BF_3{\cdot}OEt_2$ (76 μL, 0.6 mmol) was added with stirring in the dark. Soon the mixture turned yellow and later dark red. After 1 h, the mixture was cooled in an ice bath for a further 5.5 h. Then DDQ (2.029 g, 8.9 mmol) was added, and stirring was continued for 30 min. The mixture was warmed to room temperature, and the solvents were removed under reduced pressure. Purification by column chromatography with silica flash gel (first column CH_2Cl_2/hexanes, 5:1; second column $CHCl_3$; third column CH_2Cl_2/hexanes, 3:1−4:1) afforded 171 mg (6%) of the title compound as a brown-purple solid: IR (neat) $\tilde{\nu}$ 3306, 2921, 2846, 2152, 1584, 1560; ^{1}H NMR δ −2.87 (s, 2H), 4.42 (s, 4H), 7.45−7.52 (m, 2H), 7.78−7.84 (m, 4H), 8.10−8.24 (m, 8H), 8.58 (s, 2H), 8.87 (s, 8H); LD-MS obsd 1010.7 [M^+], 952.5 [M^+ − SCN], 993.3 [$M^+ - 2$ SCN], 824.2 [M^+ − SCN − I], 766.0 [$M^+ - 2$ SCN − I], 688.7 [$M^+ - 2$ SCN − I − Ph]; FAB-MS obsd 1008.0081, calcd exact mass 1008.0063 ($C_{48}H_{30}I_2N_6S_2$); λ_{abs} (toluene) 421, 515, 549, 591, 647 nm.

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Supporting Information Available: LD-MS spectra for each porphyrin, ^{1}H NMR spectra for all diamagnetic porphyrins, and ^{1}H NMR and ^{13}C NMR spectra for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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