Inverted *meso*-Aryl Porphyrins with Heteroatoms; Characterization of Thia, Selena, and Oxa N-Confused Porphyrins†

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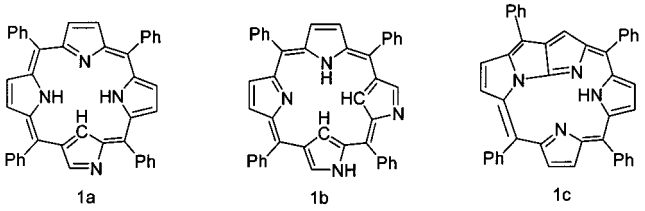
Synthesis and characterization of inverted porphyrins containing S, Se, and O are reported. A simple 3 + 1 MacDonald-type condensation using modified tripyrrane containing the N-confused ring and diols afforded various N-confused porphyrins **6a**−**f** in 19−30% yield. The single-crystal X-ray structure of **6b** shows a ruffled conformation with tilt angles of 21.11° and 31.23° for the N-confused ring and the adjacent pyrrole ring III, respectively, revealing its severe nonplanarity. Significant changes in $C_\alpha-C_\beta$, $C_\beta-C_\beta$, and $C_\alpha-X$ bond lengths are observed in **6b** relative to free thiophene and pyrrole, suggesting the altered delocalization pathway in the modified N-confused porphyrins. The two molecules in the unit cell show a cyclophane-type noncovalent dimer with a face to face orientation of two N-confused pyrrole rings as a result of the presence of weak N−H···N and C−H···N intermolecular hydrogen bonds involving pyrrole-NH, the N atom of the N-confused ring, and the C atom of the pyrrole ring. A detailed ^1H and ^{13}C NMR study by 1D and 2D methods allowed assignments of all the peaks in the free base and protonated forms. NMR studies reveal the presence of three different tautomeric forms in solution for **6c** in $CDCl_3$ at low temperature. UV−visible studies reveal absorption band shifts upon heteroatom substitution, and the magnitudes of these shifts are dependent on the nature of the heteroatom. In all cases both monoprotonated and diprotonated species have been identified, and on addition of acid, the first proton goes to the outer N2 atom of the N-confused ring

Introduction

The successful synthesis of N-confused porphyrin **1a** in 1994 independently by two groups across the globe has generated a lot of curiosity for the possible existence of new porphyrin isomers with unique properties.[1,2] More recently Furuta and co-workers have succeeded in synthesizing "doubly N-confused porphyrins"[3] **1b** and "N-fused porphyrin"[4] **1c** by appropriate synthetic modifications (Chart 1). Many research groups have recently exploited some of the unique properties exhibited by the N-confused porphyrins. Their remarkable ability to act as tetra coordinate ligands to form transition metal complexes involving a metal−carbon bond inside the porphyrin cavity has resulted in the formation of divalent simple and organometallic Ni(II) complexes,[1,5−6] trivalent Cu(III),[3] and Ag(III)[3,7] complexes with metal−carbon bonds. The surprising ease of formation of the metal−carbon bond is attributed to the presence of an Arduengo-type aromatic carbene-like structure.[8] The possible stabilization of higher oxidation states of metals by doubly N-confused porphyrin has been discussed recently by Furuta et al.[3]

Chart 1. Molecular Structures of N-Confused, Doubly N-Confused, and N-Fused Porphyrins



Core modification of N-confused porphyrin by replacing one or two pyrrole nitrogens by other heteroatoms such as O, S, and Se results in the formation of modified N-confused porphyrins with altered electronic structure.[9] The interest in such molecules lies in the fact that they form unusual metal complexes involving weak metal−heteroatom interactions leading to the isolation of some

† Dedicated to Professor Samaresh Mitra on the occasion of his 60th birthday.

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unusual complexes. Latos-Grazynski and co-workers[5,6,10] have recently isolated paramagnetic organometallic complexes of Ni(II) with an axially σ-coordinated phenyl ring using a monothiaporphyrin, a reactive Ni(II) complex having a Ni(II)−carbon equatorial bond using 21-carba porphyrin and two rare paramagnetic Ni(II) species using a methylated 21-carba porphyrin.

A perusal of literature revealed that there are only few preliminary reports on the synthesis of core-modified N-confused porphyrins in about 5−8% yield.[11] Easy and efficient synthetic methods are needed to prepare them in high yields to further exploit their unique chemistry. We have been interested in the core modification of porphyrins and expanded porphyrins and have developed efficient methods to synthesize them in multigram quantities.[12] In this paper we wish to report a high yield synthesis of core-modified N-confused porphyrins containing heteroatoms S, Se, and O by a 3 + 1 MacDonald-type condensation using appropriate precursors. In addition to synthesis, a detailed characterization of the modified porphyrins has been done using ^{1}H and 2D NMR methods, UV−visible and single-crystal X-ray structure determination. Presence of different tautomers in solution as revealed by NMR spectroscopy, adaptation of ruffled conformation in solid state and formation of a cyclophane-like dimer held by weak N−H···N intermolecular hydrogen bonds between the pyrrole NH of one porphyrin and the nitrogen of N-confused pyrrole ring of other porphyrin in packing diagram are some of the highlights of the present work.

Results and Discussion

Syntheses. Most of the synthetic methods available in the literature for the synthesis of N-confused porphyrins are based on original Rothemund reaction of benzaldehyde and pyrrole under Lewis acid catalysis.[13] For example, both Latos-Grazynski and co-workers[1] and Furuta and co-workers,[2] who independently reported the first synthesis of N-confused porphyrin, made use of the reaction of benzaldehyde and pyrrole under different conditions. Latos-Grazysnki and co-workers used $CH_2Cl_2/BF_3{\cdot}OEt_2$ while Furuta made use of *t*-BuOH/CH_2Cl_2 (1:1) in the presence of 1 equiv of concentrated HBr. Later Dolphin and co-workers[14] came up with a rational synthesis by a 2 + 2 MacDonald-type condensation using α,α-dipyrromethane dialdehyde and α,β-dipyrromethane in an overall yield of 7%. Very recently, Lindsey and co-workers[15] studied the aldehyde−pyrrole reaction under a variety of conditions and concluded that use of $BF_3{\cdot}OEt_2$ as catalyst produced more of N-confused porphyrin, while use of TFA as the catalyst gave more of ring expanded sapphyrin. Lash and co-workers also reported the synthesis of hexa- and heptaalkyl substituted inverted porphyrins by a 3 + 1 condensation of pyrrole-2,4-dicarboxaldehydes and tripyrrane dicarboxylic acid in 1% TFA/CH_2Cl_2 followed by oxidation with 0.1% $FeCl_3$.[16] Chang-Hee Lee and co-workers[11] were the first to report the synthesis of core-modified N-confused porphyrin by a 3 + 1 MacDonald approach using modified tripyrranes and 2,4-bis(α-hydroxyl methyl) substituted pyrrole. By this methodology, they were able to isolate both core-modified porphyrin and core-modified N-confused porphyrin in 3% and 8% yield, respectively. Very recently, Latos-Grazynski and co-workers[11d] reported the synthesis of 2-thia-5,10,15,20-tetraphenyl-21-carbaporphyrin (SCTPPH) with an inverted thiophene ring in 4% yield by 3 + 1 condensation of appropriate precursors. This compound on oxidation with DDQ or with excess chloranil gave 2-thia-3-oxo-5,10,15,20-tetraphenyl-21-carbaporphyrin ($SCOTPPH_2$).

In the present method, we have also followed a similar 3 + 1 approach. However, we have incorporated the N-confused pyrrole ring as a part of tripyrrane unit and used core-modified diols using *p*-toluene sulfonic acid (*p*-TsOH) as catalyst in dichloromethane followed by oxidation with chloranil (Scheme 1). Thus **2** on reduction with LAH in THF at 0 °C gave **3**, which on treatment with pyrrole and TFA gave the key precursor ***4;*** **4** was further reacted with different diols **5a**−**d** in dichloromethane using 0.1 equiv of *p*-TsOH as the catalyst followed by oxidation with chloranil to afford the desired N-confused porphyrins **6a**−**f**. It is pertinent to point out here that the concentration of *p*-TsOH is crucial for the high yields of N-confused porphyrin. Use of 0.1 equiv gave maximum yield and higher concentrations of *p*-TsOH resulted in the formation of normal core-modified porphyrin. The obvious advantages of this method lies in the following two observations: (a) exclusive formation of the desired

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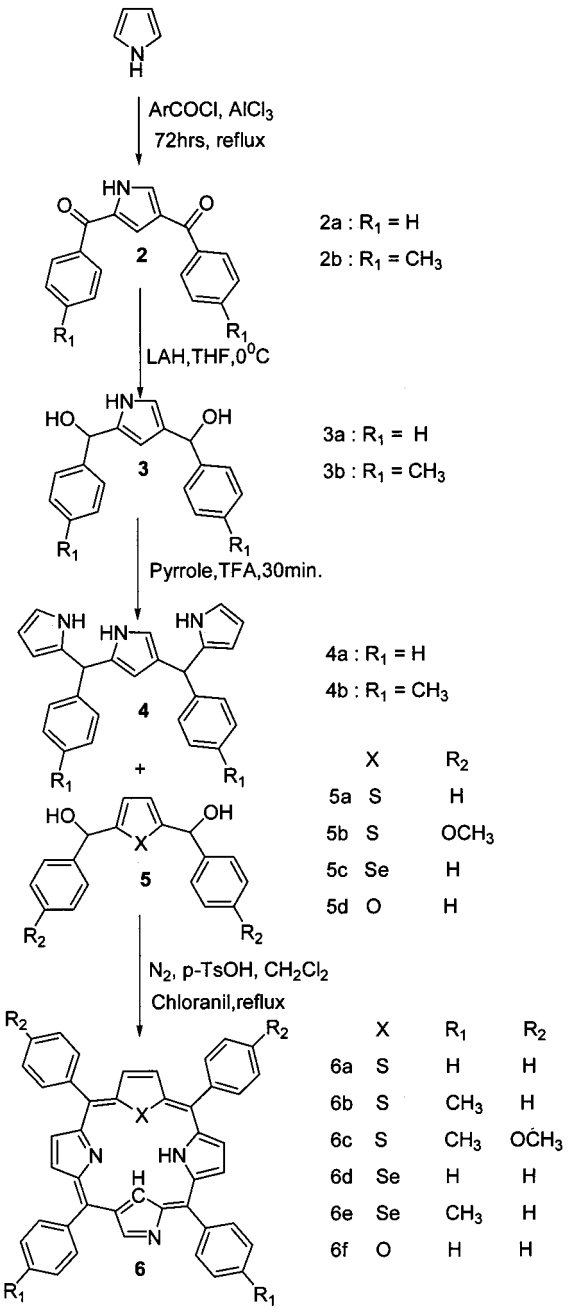
Scheme 1. Synthesis of Core-Modified N-Confused Porphyrins



core-modified N-confused porphyrin with only a trace amount of normal porphyrin, making the separation on column very easy and (b) formation of the desired products in high yields; for example **6a**−**c** were isolated in 28−32%, **6d** in 29%, and **6f** in 19%. This is in contrast to 8% and 5.5% yield reported for **6a** and **6f**, respectively, by the earlier method.[11a,b]

NMR Studies. Detailed ^{1}H and ^{13}C NMR spectra were recorded for both free base and protonated forms to arrive at the solution structure of the porphyrins **6a**−**f**. As an example most of the ^{1}H and ^{13}C NMR assignments were done on **6c** in its protonated form at 298 K; observation of all signals with better resolution were seen in the ^{1}H NMR spectrum and best spectral dispersion was obtained in ^{13}C NMR. Wherever difficulties in assignments arose, help was rendered from spectral information obtained at 243 K and 223 K. These assignments were then correlated with the free base form of **6c** at 298 K, as only specific shifts of resonances of the core ring protons and phenyl protons were observed on protonation. Figure 1 gives a comparison of ^{1}H NMR spectra of **6c** in its free base and protonated forms at 298 K and low temperatures. The detailed ^{1}H and ^{13}C peak assignments were carried out by combined use of homonuclear, heteronuclear one-bond and long-range correlation.[17] The numbering of the compound along with the correlation observed is as shown in Figure 2.

The ^{1}H NMR spectrum (at 298 K) of the protonated **6c** showed a singlet at −1.76 ppm, a broad resonance at 1.86 ppm (obtained at 243 K), a doublet at 2.64 ppm and a singlet at 4.03 ppm. In the aromatic region, a doublet at 7.35 ppm and multiplet between 7.73 and 8.21 ppm, two well-separated doublets at 8.42 and 8.51 ppm, and a strongly coupled spin system at 8.95 ppm were observed. The specific assignments of these protons were based on ^{1}H−^{1}H COSY recorded for **6c** in its freebase and protonated forms. The outer 3-CH proton of the N-confused pyrrole ring was assigned to the peak at 8.21 ppm since it showed a cross-peak in the COSY spectrum with 2-NH proton at 12.58 ppm. The peak at −1.76 ppm was assigned to inner 21-CH proton. This was further confirmed by the presence of cross-peak between 2-NH proton at 12.58 ppm and the 21-CH at −1.76 ppm. Regarding the assignments of the other two-pyrrole units and its differentiation with the thiophene spin system, a combination of homonuclear, heteronuclear one-bond and long-range correlations were employed. On the basis of the homonuclear *J*-correlation experiment done at 243 K, the broad signal at 1.86 ppm gave cross-peaks with the two doublets at 8.42 and 8.51 ppm, confirming both the NH's at 1.86 ppm and the two CH protons of the pyrrole units I and III, respectively. Hence the strongly coupled spin system centered at 8.95 ppm was ascribed to both the CH protons of the thiophene ring. The two pyrrole units showed a typical COSY pattern and they had one set of protons centered at 8.17 and 8.19 ppm and the other at 8.42 and 8.51 ppm, respectively. The differentiation of the pyrrole units was done based on the HMBC and HMQC data. The outer 3-CH proton of N-confused pyrrole at 8.21 ppm showed a long-range correlation at 152.97 ppm, which further matched the long-range correlation by the CH proton of the pyrrole resonating at 8.51 ppm, thus differentiating the remaining two pyrrole units. Similarly, CH proton of the other pyrrole unit at 8.17 ppm gave a long-range correlation with CH carbon at 132.66 ppm as well as to the quaternary carbon at 152.97 ppm. The chemical shift of the quaternary carbon at 152.97 ppm also showed long-range correlation with the thiophene CH proton, confirming once again the assignments of both the pyrrole protons. This quaternary carbon was identified to be C-15 and hence the protons of the pyrrole unit I were confirmed to be the ones that resonate at 8.17 and 8.42 ppm (attached to C-17 and C-18, respectively). Subsequently, all the other quaternary carbons were assigned on the basis of similar such analyses. Further assignments of the phenyls, methyl, methoxy, and quaternary carbons were then straightforward.

The signal due to 24-NH proton was not observed for the free base form of **6c** at 298 K, suggesting a rapid

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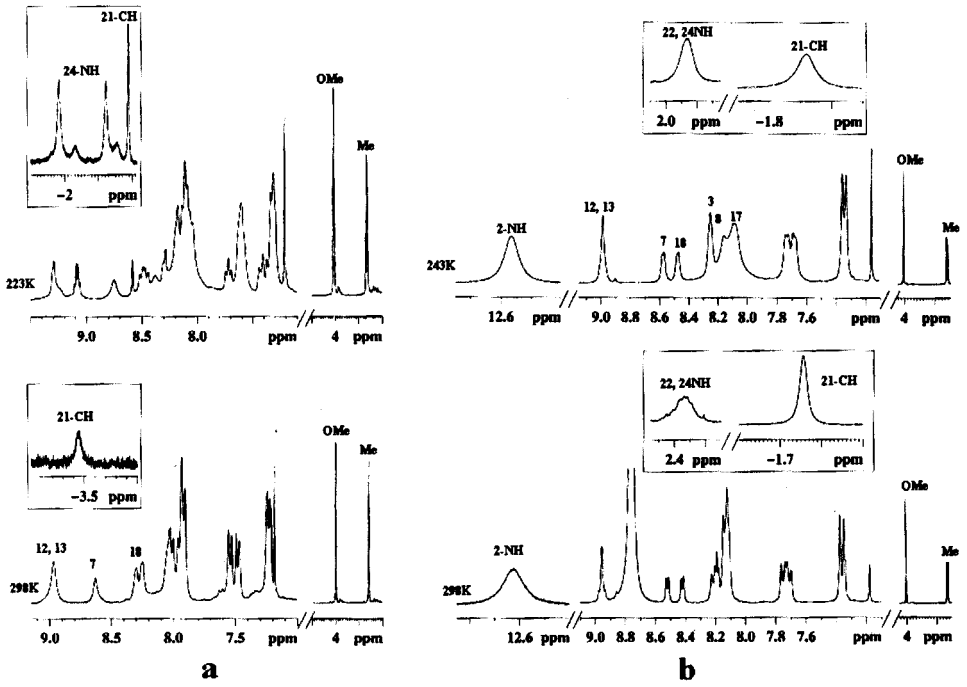


Figure 1. ^{1}H NMR spectra of **6c**: (a) free base and (b) its diprotonated form at room and low temperature in $CDCl_3$.

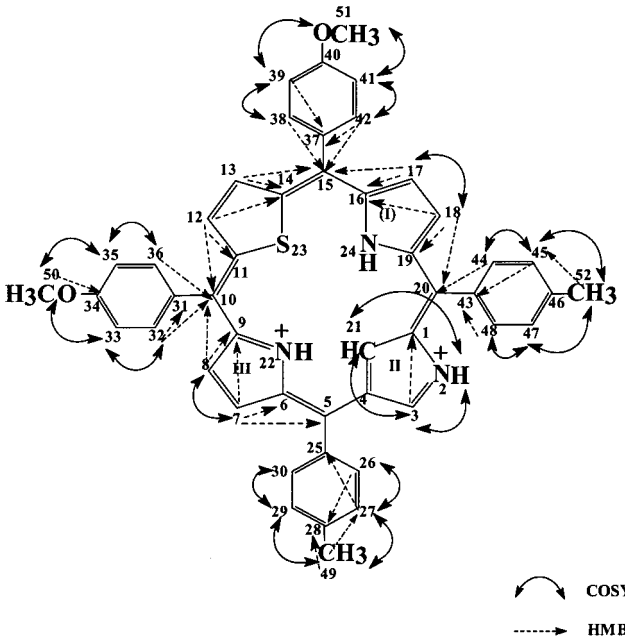
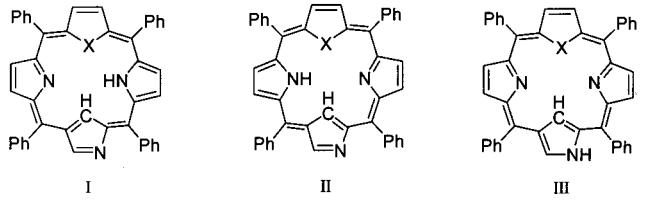


Figure 2. The numbering and *J* and HMBC correlation observed for **6c**.

tautomerism where this proton is exchanging sites between the two pyrrole nitrogens. However on cooling the sample to 223 K multiple sets of signal were obtained (Figure 1a, 223 K). This dynamic behavior was further probed by recording the NOESY spectrum at 223 K, which revealed the following: (i) The 21-CH signal at −3.95 ppm gave a NOE correlation to the 24-NH at 1.02 ppm, thus confirming that these two pyrrole units are not experiencing any major ring flipping. (ii) Interestingly, three sets of paired resonances assigned to 22-NH on pyrrole ring III observed at −3.54, −3.21, −2.30, −1.83, 2.18, and 1.90 ppm showed chemical exchange phenomena among themselves suggesting the presence of different tautomers in solution. We attribute the

Chart 2. Possible Tautomers for 6a−f



presence of multiple sets of peaks for the NH protons to the existence of different tautomers in equilibrium in solution. Three different tautomeric structures (Chart 2) can be envisaged depending on the location of the proton. In tautomers II and I, the hydrogen is located on the either of inner pyrrole nitrogens, whereas in III, the proton is located on the nitrogen of the N-confused ring. The observation of three sets of peaks at 223 K suggest the presence of three tautomers I, II, and III in solution in equilibrium. Justification for such a interpretation also comes from the studies of Chang-Hee Lee and coworkers[11c] on the thia derivative. On the basis of the NMR observations, they have also suggested the presence of three different tautomers in equilibrium. However, the protonated form does not show this behavior. The extensive NMR studies of **6c** were then used for the assignments of peaks in compounds **6a**, **6b**, **6d**, and **6f**. However we should mention here that for compounds **6a**, **6d**, **6e**, and **6f** the inner NH signal in its free base form was not observed up to 223 K, suggesting the presence of rapid tautomerism even at such low temperature.

The protonated form of **6e** behaved slightly different from others. Figure 3 shows the temperature-dependent spectra of **6e** in its protonated form. It is clear from the figure that the two inner-22,24-NH signals and outer 2-NH signal were not observed at room temperature, However at 243 K, two separate signals for 22,24-NH protons were observed at 3.09 and 2.99 ppm, suggesting the nonequivalence of these protons. The outer 2-NH signal is also clearly seen at 243 K at 13.49 ppm. Also it is seen from the spectrum that the selenophene protons

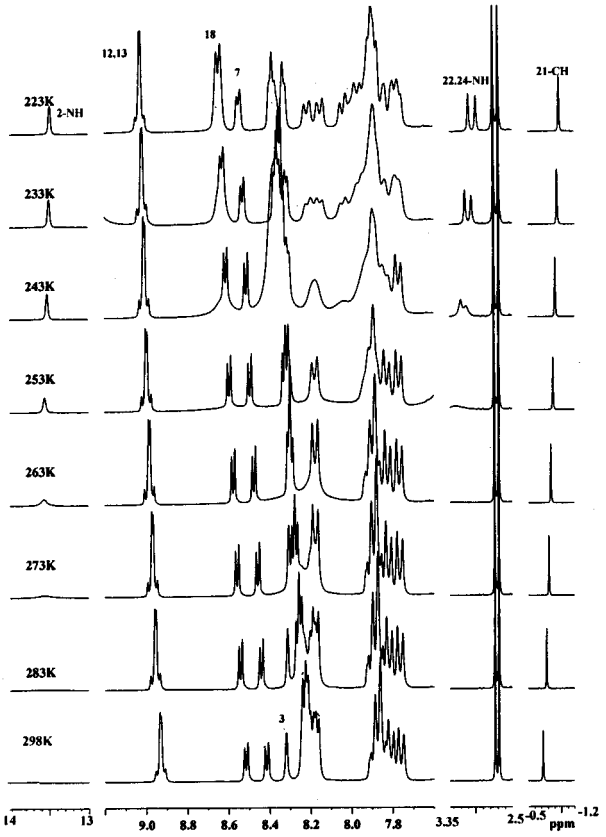


Figure 3. Temperature-dependent ^{1}H NMR spectra of the diprotonated form of **6e** in $CDCl_3$.

are strongly coupled resulting in the appearance of two overlapping doublets at 8.95 ppm. From the COSY spectrum, it was observed that the inner 21-CH is strongly coupled to outer 3-CH of the confused pyrrole ring as observed in the case of normal N-confused porphyrin.[1]

NH Tautomerism in Free Base N-Confused Porphyrins. Chang-Hee Lee and co-workers,[11c] who reported the first synthesis of **6a** and **6f**, have shown the existence of different tautomers forms for **6a** and **6f**. Specifically, **6f** exhibit only one stable tautomer where the inner proton is present on the inner pyrrole nitrogen as in I (Chart 2). However, the thia derivatives **6a** exist as two tautomers at room temperature, the major tautomer where the proton is located on the outer nitrogen of the N-confused ring as in III and a minor tautomer where the proton is on the inner pyrrole nitrogen as in I. Further, at 223 K, a third tautomer was identified where the proton is on the other inner pyrrole nitrogen as in II and the ratio of the three tautomers was found to be 1:1:10.5/III:I:II.

In the present study, the detailed proton NMR analysis of the free base derivatives and the protonated derivatives support the conclusions of Chang-Hee Lee, for the oxa derivative **6f** where there is only one dominant tautomer as in I. However, for the thia derivative **6a**, results support that the major tautomer is the one in which the proton is located on the inner pyrrole nitrogen as in I rather than in III. Strong support for such a conclusion is based on the following observations: (i) the inner NH signals are seen in the shielded region, (ii) the outer NH signal is seen in the region 12−13 ppm at room temperature only on careful titration of free bases with a dilute solution of TFA, and (iii) the presence of strong hydrogen bonding interaction between the inner NH of one molecule and the outer nitrogen of the other molecule forming a cyclophane-type dimer in the unit cell of the single-crystal X-ray structure of **6b**. However, at lower temperature the results are in agreement with that of Chang-Hee Lee and co-workers, where all the three tautomers are in equilibrium for **6a**.

Table 1. Selected Bond Distances for 6b and Their Comparison with Free Thiophene and Pyrrole Units.

ring	$C_\alpha-X^{\#}$ (Å)	$C_\alpha-C_\beta$ (Å)	$C_\beta-C_\beta$ (Å)
thiophene	1.766(3), 1.759(3)	1.436(4), 1.422(4)	1.366(4)
pyrrole I	1.336(4), 1.383(3)	1.454(3), 1.460(4)	1.353(4)
inv pyrrole II	1.336(3), 1.416(4)	1.408(4), 1.415(4)	1.390(3)
pyrrole III	1.343(4), 1.381(4)	1.439(4), 1.460(4)	1.357(4)
free thiophene	1.714	1.370	1.423
free pyrrole	1.370	1.382	1.417

Structural Characterization. Further proof for the proposed structure came from the single-crystal X-ray structure of **6b**, which is shown in Figure 4. In the structure, the imino hydrogen atom could not be assigned unequivocally to either of N1 or N3 as a result of rapid interconversion of NH tautomers during the time required for the measurements (supported by ^{1}H NMR data, vide infra). Our analysis suggests a 50% probability of occupation on each nitrogen.[5]

The structure (Figure 4) reveals the nonplanarity of the macrocycle in a ruffled conformation[18] where the meso carbons are found alternatively above and below the mean plane defined by four meso carbon atoms. The specific deviations from the planarity are C5, −0.050(1); C10, 0.055(1); C15, −0.051(1); and C20, −0.051(1) Å. The deviation of core heteroatoms S, N1, N3, and C13 are −0.087(2), −0.069(3), −0.016(3), and 0.21(3) Å, respectively, revealing the maximum deviation for the C-13 atom of N-confused ring. The nonplanarity is also clearly reflected in the dihedral angles of the planes of individual pyrrole (heterocyclic) rings with respect to the mean plane defined by four meso carbon atoms. They are 2.82(6)° for the thiophene ring, 21.11(9)° for the N-confused pyrrole ring, and 15.77(9)° and 31.23(9)° for the two opposite pyrrole rings. A comparison of these angles with that of N-confused porphyrin suggest that in the N-confused porphyrin, the N-confused pyrrole ring shows maximum deviation (26.9°),[2] while in **6b** both N-confused pyrrole ring and one of the adjacent pyrrole ring show maximum deviation. This can be understood in terms of the substitution of the large sulfur atom in the place of nitrogen increasing the repulsion between the inner N−H and the sulfur atom, as a result of which the pyrrole ring is forced to be tilted away from the mean plane.[11b]

Table 1 lists the relevant bond distances of heterocyclic rings in the macrocycle **6b** and in the free thiophene and pyrrole rings. Substitution of pyrrole NH by thiophene sulfur changes the π-delocalization, and the bond distances are altered accordingly. For example, there is a significant increase (0.058 Å) in the $C_\alpha-S$ distance while $C_\beta-C_\beta$ distance experience a significant decrease (0.057 Å) in **6b** relative to the free thiophene revealing that the π-delocalization through the thiophene ring is altered in **6b**. Furthermore, comparison of $C_\alpha-S$, $C_\alpha-C_\beta$, and $C_\beta-C_\beta$ distances of **6b** with that of the 5,10,15,20-tetraphenyl-

(18) Scheidt, W. R., Lee Y. J. In *Structure and Bonding*; Buchler, J. W., Ed.; Springer-Verlag: Berlin, Heidelberg, 1987; Vol.64, p 1.

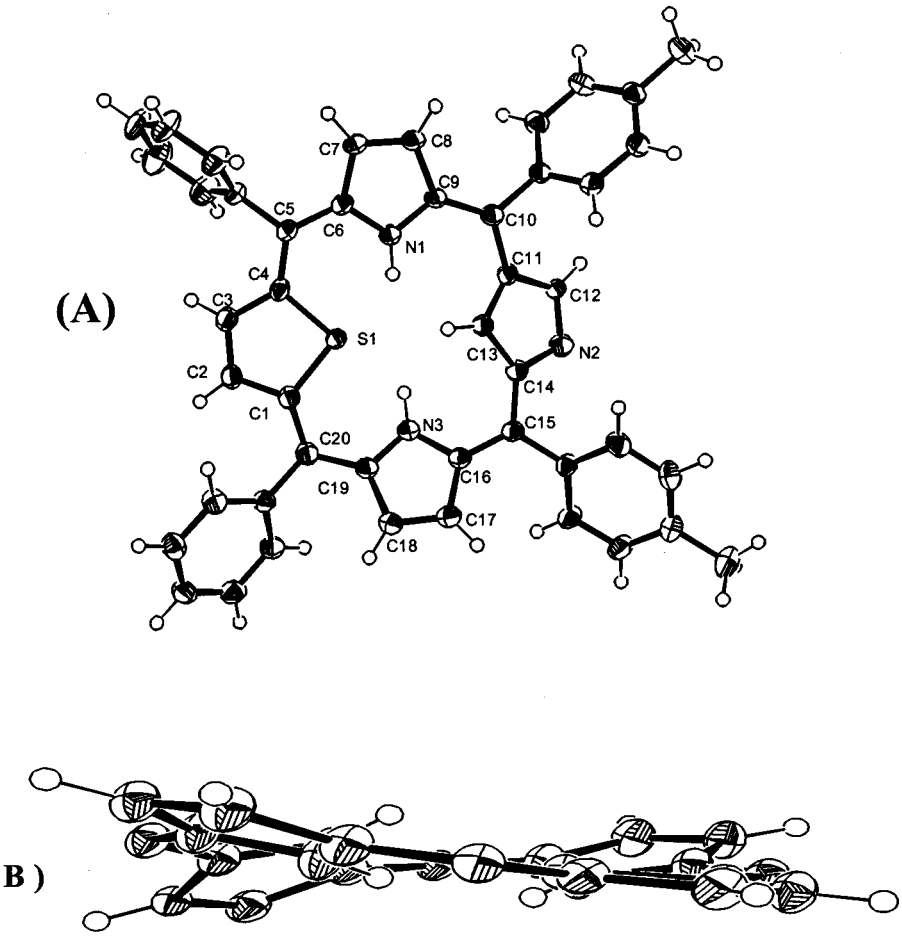


Figure 4. ORTEP diagram of **6b**: (a) plane view and (b) side view. Phenyl rings are omitted for clarity in side view.

21-thiaporphyrin (1.748(4), 1.408(6), and 1.367(7) Å, respectively)[19] indicate significant increases for $C_\alpha-S$ and $C_\alpha-C_\beta$ distances in **6b**, suggesting that the presence of N-confused ring further alters the delocalization pathway. The differences in the two types of pyrrole rings (N-confused and normal) are also reflected in the bond distances; the $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ distances of the N-confused ring are significantly lower and higher respectively relative to normal pyrrole ring again suggesting the modified electron delocalization pathway. The aromatic nature of **6b** is evident from the observation that $C_\alpha-C_\beta$ distances are higher than the $C_\beta-C_\beta$ distances.[20] Because of the bigger sulfur atom the core size of **6b** is restricted and this is reflected in the nonbonded distances: $S-C_\beta = 3.452$ Å and N1−N3 = 4.599 Å and these distances compare well with those observed for 5,10,15,-20-tetraphenyl-21-thiaporphyrin (S−N2 = 3.546 (8) Å, N1−N3 = 4.40(1) Å).[19]

A close look at the packing diagram (Figure 5) reveals another interesting aspect of the structure. There are two molecules in the unit cell and these molecules are linked to each other through a noncovalent weak N−H···N and C−H···N intermolecular hydrogen bonds involving the pyrrole-NH, the N atom of the N-confused ring and C atom of pyrrole ring. Four such interactions produce a cyclophane-like dimeric structure where the two N-confused rings are almost one above the other. The N−H···N distance of 3.14 (4) Å, bond angle 117.2° and C−H···N distance of 3.24 Å, bond angle 128.25° are in the range expected for N−H···N and C−H···N hydrogen bonds reported in the literature.[21] Also, there are two intramolecular N−H···S hydrogen bonds and one C−H···S hydrogen bond in each molecule between pyrrole N1-H, N3-H, pyrrole C-13, and thiophene sulfur with an average distance of 2.74 and 3.45 Å for N−H···S and C−H···S hydrogen bonds, respectively.

UV−Visible Studies. All the modified porphyrins **6a−f** in their free base form exhibit split Soret band in the region 425−450 nm and Q-bands in the region 500−750 nm. UV−visible data are tabulated in Table 2. The effect of heteroatom substitution is seen in the red shift of absorption bands relative to NCTPP[1,2] and the magnitudes of the shifts are dependent on the nature of the heteroatom. The presence of split Soret reveals lower symmetry in N-confused porphyrins relative to the parent *meso*-tetraphenyl porphyrin (H_2TPP). Stepwise protonation results in the further red shifts of Soret and Q-bands, which is typical of *meso*-aryl porphyrins.[22] However the magnitude of shifts of Q-bands are much larger (for example, Q-1 band shifts fall in the range of 80−140 nm) for the N-confused porphyrins relative to $[H_4TPP]^{2+}$ (the Q-1 band shifts only 12 nm upon protonation of H_2TPP),[23]

(19) Latos-Grazynski, L.; Lisowski, J.; Szterenberg, L.; Olmstead, M. M.; Balch, A. L. *J. Org. Chem.* **1991**, *56*, 4043.

(20) Sessler, J. L.; Morishima, T.; Lynch, V. *Angew. Chem.* **1991**, *103*, 1018; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 977.

(21) (a) Jeffrey, G. A.; Saenger, W. In *Hydrogen Bonding in Biological Structure*; Springer-Verlag: Berlin, 1994; p 29. (b) Desiraju, G. R. *Angew. Chem.* **1995**, *107*, 2541; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

(22) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, p 1.

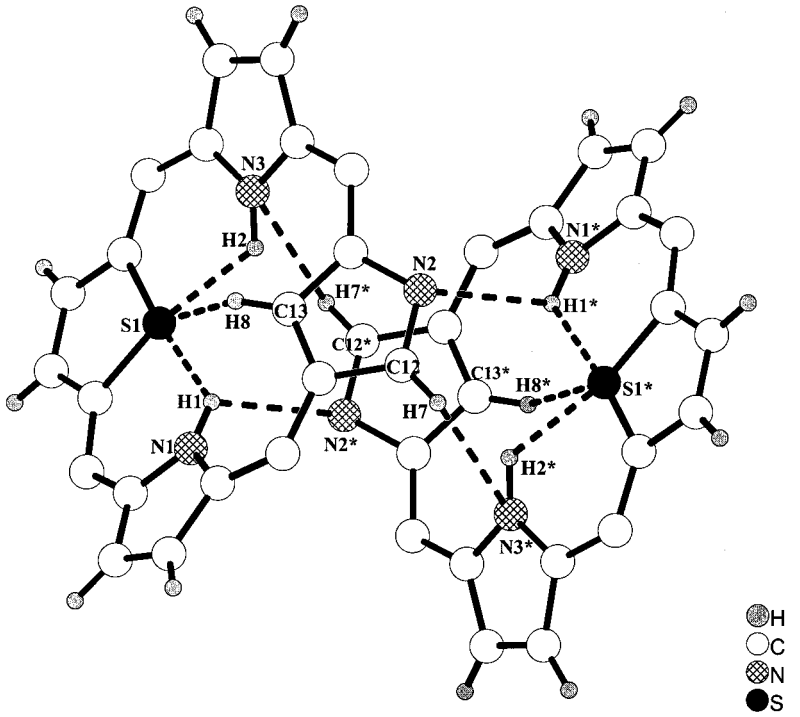


Figure 5. Packing diagram of **6b** showing interactions between the two molecules through intermolecular and intramolecular hydrogen bonds. The hydrogen bonds are marked with dotted lines.

Table 2. UV−Vis Data for N-Confused Porphyrins in Their Free Base, Mono-, and Diprotonated State in Dichloromethane.

porphyrin	Soret band, λ_{max} (nm) ($\times 10^{-4}$) ($dm^3\ cm^{-1}\ mol^{-1}$)	Q-bands, λ_{max} (nm) ($\times 10^{-3}$) ($dm^3\ cm^{-1}\ mol^{-1}$)
N-CTPP	383(sh), 440(9.68)	506(4.7), 543(7.5), 585(10.9), 672(2.8), 730(9.7).
6a	431(sh), 446(50.96).	550(47.73), 586(48.22), 624(57.33), 674(52.11), 729(17.89).
6a·H^+	445(42.1), 478(39.17).	562(74.19), 611(59.31), 687(62.50), 744(84.70).
6a·$2H^+$	471(78.34)	708(106), 813(111.96).
6b	429(sh)(35.72), 446(51.6).	554(26.670), 591(31.56), 625(44.03), 676(42.43), 733(6.84).
6b·H^+	449(40.02), 477(44.97).	563(47.94), 614(39.56), 740(82.49), 826(37.94).
6b·H^+	472(91.43)	710(111.19), 816(100.76).
6c	430(sh), 447(36.89)	553(28.12), 597(28.0), 630(33.56), 680(31.59), 724(10.31).
6c·H^+	450(41.65), 477(46.08).	562(58.28), 616(48.32), 742(96.76).
6c·$2H^+$	480(51.08)	741(91.1), 864(80.78).
6d	432(sh), 449(47.21)	543(16.36), 579(32.06), 617(55.34), 664(57.01), 742(8.79).
6d·H^+	440(41.61), 485(54.34).	572(53.11), 628(53.05), 745(147.98), 808(61.93).
6d·$2H^+$	481(73.84)	740(123.42), 836(95.10)
6e	434(sh), 449(29.0)	578(47.27), 615(51.18), 664(45.54), 728(18.6).
6e·H^+	441(25.42), 487(26.36).	574(57.92), 670(95.89), 748(59.64).
6e·$2H^+$	420(sh), 482(43.11)	744(109.89), 823(90.63).
6f	428(sh), 440(65.03)	476(31.22), 545(10.39), 582(6.78), 651(4.28), 724(4.05).

suggesting a severe distortion from planarity upon protonation. The observed ruffled structure in the solid state for the free base also supports such a conclusion. Addition of first proton to the free base form can either go to inner N-22 nitrogen or outer N-2 atom to produce a monoprotonated species. Careful titration experiments using dilute TFA solution in the ^1H NMR spectrum results in the appearance of a peak in the region 12.56−14 ppm for **6a**−**f** suggesting that site of first proton addition is outer N-2 atom of the confused pyrrole ring. The second proton obviously goes to the inner N-22 atom and the appearance of peaks in the shielded region (1.8−3.1 ppm) justifies such a conclusion. The protonation shown in Scheme 2 is essentially same as that observed for the N-confused porphyrin,[1] suggesting that the heteroatom substitution does not alter the protonation sites.

Conclusions

Syntheses of heteroatom containing N-confused porphyrins **6a**−**f** has been achieved in high yields by a 3 + 1 condensation of appropriate precursors using 0.1 equiv of *p*-TsOH as the catalyst. Substitution of a heteroatom into the core of N-confused porphyrins alters the electronic structure of the ring, and this is reflected in the altered spectroscopic and structural properties. The X-ray structure of **6b** reported here represents the first single-crystal structural characterization of a core-modified N-confused porphyrin. It is hoped that the availability of multigram quantities of these new core-modified N-confused porphyrins will allow further exploitation of their rich chemistry in terms of their coordination behavior toward transition metals and their use as catalysts for organic transformations. Studies in this direction are in progress in this laboratory.

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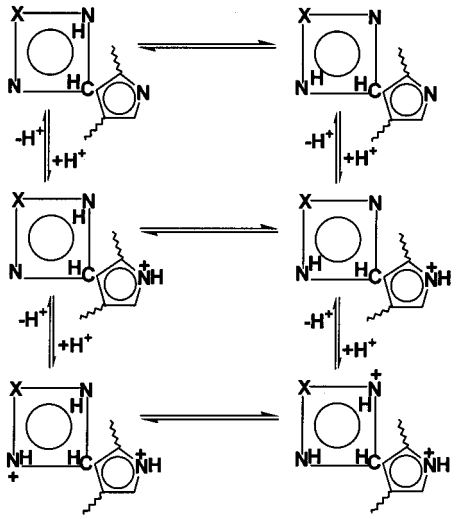
Scheme 2. Stepwise Protonation of Core-Modified N-Confused Porphyrins



Experimental Section

All of the chemicals used for the synthesis were reagent grade unless otherwise specified. Solvents for spectroscopic measurements were purified and dried according to the standard methods.^{1}H and ^{13}C NMR spectra were measured on a 300 or 500 MHz Bruker spectrometer or 400 MHz JEOL spectrometer in $CDCl_3$ or CD_2Cl_2 solution. FAB mass spectra were obtained from a JEOL SX-120/DA6000, and EIMS was obtained from JEOL D-300 Spectrometer. The electrospray mass spectra were recorded on a MICROMASS QUANTRO II triple quadrupole mass spectrometer; C, H, N analyses were done on a Heraeus Carlo Erba 1108 elemental analyzer. The UV−vis spectra were recorded on a Perkin-Elmer Lambda 20 UV−vis spectrophotometer. Crystal measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a rotating anode generator, and the crystal was mounted on a glass fiber. The crystal to detector distance was 235 mm and all calculations were performed using teXsan[24] crystallographic software package of the Molecular Structure Corporation.

Syntheses. Compound **4a** was prepared by the method reported earlier by Chang-Hee Lee et al. [11a] and **5a**−**d** were prepared using the methodology reported earlier from this laboratory. [12e,g]

5,10-Ditolyl-8-aza-16-carba-5,10,15,17-tetrahydrotripyrrane 4b. This compound was obtained by the Friedel-Craft reaction. Pyrrole (3.5 g, 0.05mol) by *p*-methyl-benzoyl chloride (18 g, 0.12mol) in the presence anhydrous $AlCl_3$ (15.6 g, 0.12mol) for 72 h under reflux gave 2,4-bis(*p*-methyl)-benzoyl-pyrrole (6 g, 44%) **2b**. One gram of **2b** (3.63 mmol) was then reduced with $LiAlH_4$ (0.55 g, 0.02 mmol) by stirring it in the N_2 atmosphere for 2 h at 0 °C in dry THF, which gave 2,4-bis(*p*-methyl-phenyl hydroxy methyl)-pyrrole **3b**, which was extracted with dichloromethane and dried over sodium sulfate. The solvent removed at room temperature by vacuum and was immediately reacted with excess pyrrole in the presence of trifluoro acetic acid (TFA) (0.06 g, 0.5 mmol). The reaction mixture was quenched with dichloromethane and neutralized by treating it with 0.1 N NaOH solution. The organic layer separated was given a water wash for two times and dried over sodium sulfate. The excess solvent was removed by vacuum at room temperature and the compound was purified by silica gel column.The yellow band moving with ethyl acetate and petroleum ether (11:89) was the desired product **4b** (0.6 g, 41%). EI mass: *m*/*z* (%) 405(49.2) $[M]^+$. Anal. Calcd for $C_{28}H_{27}N_3$: C 82.92, H 6.71, N 10.37. Found: C 82.94, H 6.73, N 10.43. ^{1}H NMR (400 Hz/$CDCl_3$): δ 7.69−7.67 (m, 2H), 7.48-(s, 1H), 7.06−6.78(m, 8H), 6.46(s, 2H), 6.06(s, 1H), 5.97−5.95-(m, 2H), 5.66(s, 2H), 5.62(s, 1H) 5.14(s, 1H), 5.01(s, 1H), 2.23(s, 3H), 2.18(s, 3H).

2-Aza-21-carba-23-thia-5,10,15,20-tetraphenyl Porphyrin 6a. 2,5-Bis(phenyl hydroxy methyl) thiophene **5a** (0.3 g, 1.01 mmol) and 5,10-diphenyl-8-aza-16-carba-5,10,15,17-tetrahydrotripyrrane **4a** (0.38 g, 1.01 mmol) were dissolved in 500 mL of dry dichloromethane and stirred in nitrogen atmosphere for 10 min. *p*-Toluene sulfonic acid (*p*-TsOH) (0.02 g, 0.10 mmol) was added into it and allowed to stir for another 90 min under dark at room temperature. Chloranil was added and the reaction mixture was opened to air and was refluxed for 90 min. The reaction mixture was cooled, solvent was removed by distillation, and the compound was purified by basic alumina column. Column chromatography yielded traces of 2-aza-21-carba-5,10,15,20-tetraphenyl porphyrin (NCTPP) and normal monothia porphyrin (STPPH). The desired product **6a** was eluted with ethyl acetate and dichloromethane mixture (1:44) and shiny bluish green crystals of the compound was obtained from dichloromethane and *n*-hexane mixture (0.17 g, 26%), which decomposes above 300 °C. At higher concentration of *p*-TsOH, the tripyrrane has undergone acidolysis and gave only STPPH and traces of NCTPP. MS (electro spray): *m*/*z* (%) 632.3 (100) $[M]^+$. Anal. Calcd for $C_{44}H_{29}N_3S$: C 83.65, H 4.63, N 6.65. Found: C 83.92, H 4.73, N 6.85. ^{1}H NMR (500 MHz, CD_2Cl_2, 193K): δ 11.23 (br s, 1H), 8.56 (br s, 3H), 8.26 (br s, 7H), 8.0−7.64 (m, 16H). ^{1}H NMR (500 MHz,CD_2Cl_2): δ at 223K 13.62 (s, 1H), 9.14−9.13(d, 2H, J = 4.5 Hz), 8.68 (s, 1H), 8.57 (s, 1H), 8.49 (s, 1H), 8.34−8.31(m, 6H), 8.02−7.89 (m, 16H), −1.98(s, 1H).

2-Aza-21-carba-23-thia-5,20-di-*p*-tolyl-10,15-diphenyl Porphyrin 6b. 2,5-Bis(phenyl hydroxy methyl) thiophene **5a** (0.40 g, 1.35 mmol) and **4a** (0.55 g, 1.35 mmol) were dissolved in 500 mL of dry dichloromethane in the presence of *p*-TsOH (0.03 g, 0.14 mmol) and reacted with chloranil (0.50 g, 2.02 mmol) as explained above. The desired product **6b** was eluted with ethyl acetate and dichloromethane mixture (1:99) and shiny bluish green crystals of the compound were obtained from dichloromethane and *n*-hexane mixture (0.25 g, 28%), which decomposes above 300 °C. FAB mass *m*/*z* (%): 660 (50) $[M]^+$. Anal. Calcd for $C_{46}H_{33}N_3S$: C 83.73, H 5.04, N 6.36. Found: C 83.56, H 5.32, N 6.21%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.55 (br s, 1H**),** 8.27 (br s, 1H), 7.92−7.87 (m, 8H), 7.68−7.62 (m, 6H), 7.52−7.50 (d, 2H, J = 7.5 Hz), 7.47−7.46 (d, 2H, J = 7 Hz), 2.61 (s, 6H) and at 193 K four broad peaks as a result of paired resonance at −3.65, −3.15, −2.35, −1.85 and a broad singlet which appears at 11.19 ppm. ^{1}H NMR (500 MHz, CD_2Cl_2/TFA, 298 K): δ 9.05−9.02 (m, 2H), 8.59−8.58 (d, 1H, J = 4.5 Hz), 8.49−8.48 (d, 1H, J = 4.5 Hz), 8.24 (s, 1H), 8.23−8.18 (m, 12H), 7.92−7.88 (m, 4H), 7.85−7.84 (d, 2H, J = 7.5 Hz), 7. 81−7.8(d, 2H, J = 7.5 Hz), 2.74 (s, 3H), 2.7 (s, 3H), −1.36 (s, 1H) and 13.41 (s, 1H) at 203 K.

2-Aza-21-carba-23-thia-5,20-di-*p*-tolyl-10,15-di-*p*-methoxy-phenyl Porphyrin 6c. Compound **4b** (0.36 g, 8.96 mmol) and 5-bis(*p*-methoxy-phenyl hydroxy methyl) thiophene **5c** (0.32 g, 8.96 mmol), *p*-TsOH (0.02 g, 0.90 mmol), and chloranil-(0.33 g, 1.34 mmol) under similar reaction conditions as mentioned above gave lustrous bluish green solid identified as **6c**. This was purified by basic alumina column. The desired product was eluted with ethyl acetate and dichloromethane (4:96) mixture and was recrystallized from dichloromethane/*n*-hexane mixture (0.20 g, 30%), which decomposes above 300 °C. FAB mass *m*/*z* (%): 720 (100) $[M]^+$. Anal. Calcd for $C_{48}H_{37}N_3O_2S$: C 80.08, H 5.18, N 5.84. Found: C 80.22, H 5.41, N 5.67. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) ppm: as shown in Table 1.

2-Aza-21-carba-23-selena-5,10,15,20-tetraphenyl Porphyrin 6d. 2,5-Bis(phenyl hydroxy methyl) selenophene **5c** (0.41 g, 1.20 mmol) and **4a** (0.38 g, 1.10 mmol), *p*-TsOH (0.02 g, 0.11 mmol), and chloranil (0.54 g, 2.19 mmol) under similar reaction conditions explained above gave bluish green solid identified as **6d** on basic alumina column with ethyl acetate and dichloromethane (4:41) mixture as eluent. The bluish green lustrous solid was recrystallized in dichloromethane and *n*-hexane mixture (0.20 g, 26%), which decomposes above 300

(24) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1999)

°C. MS (electro spray) *m*/*z* (%): 680 (70) $[M + 1]^+$. Anal. Calcd for $C_{44}H_{29}N_3Se$: C 77.87, H 4.31, N 6.19. Found: C 77.17, H 4.21, N 6.36. ^{1}H NMR (500 MHz, $CDCl_3$, 223 K): δ 9.79 (s, 1H), 8.63 (s, 2H), 7.99 (s, 1H), 7.97−7.85 (m, 10H), 7.72−7.61-(m, 15H).^{1}H NMR (500 MHz, $CDCl_3$/TFA, 223 K): δ 13.23 (s, 1H), 9.05−9.01 (m, 2H), 8.65−8.64 (d, 2H, J = 4 Hz), 8.54−8.53 (d, 1H, J = 4 Hz), 8.46−8.45 (d, 1H, J = 7 Hz), 8.39−8.35 (m, 2H), 8.31−8.3 (d, 1H, J = 6 Hz), 8.27 (s, 1H), 8.25−8.24 (d, 1H, J = 3 Hz), 8.12 (s, 2H), 8.02−7.73 (m, 16H), −1.32(s, 1H).

2-Aza-21-carba-23-selena-5,20-di-*p*-tolyl-10,15-diphenyl Porphyrin 6e. 2,5-Bis(phenyl hydroxy methyl) selenophene **5c** (0.3 g, 0.87 mmol), **4b** (0.35 g, 0.87 mmol), *p*-toluene sulfonic acid (0.02 g, 0.09 mmol), and chloranil (0.32 g, 1.32 mmol) under similar reaction conditions as above gave a bluish green solid identified as **6e** on basic alumina column with ethyl acetate and dichloromethane (6:94) mixture as eluent. The bluish green lustrous solid was recrystallized in dichloromethane and *n*-hexane mixture (0.18 g, 29%), which decomposes above 300 °C. FAB mass *m*/*z* (%): 706 (70) $[M + 1]^+$. Anal. Calcd for $C_{46}H_{33}N_3Se$: C 78.17, H 4.7, N 5.94. Found: C 78.36, H 4.81, N 6.09. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 9.38 (br s, 2H), 8.52 (s, 2H), 7.91−7.83 (m, 8H), 7.80 (s, 1H), 7.70−7.54 (m, 8H), 7.5−7.48 (d, 2H, J = 8.05 Hz), 7.44−7.41 (d, 2H, J = 8.05 Hz), 2.6 (s, 3H), 2.58 (s, 3H). ^{1}HNMR (300 MHz, $CDCl_3$/TFA, 298 K): 8.95−8.91 (m, 2H, J = 5.85 Hz), 8.52−8.51(d, 1H, J = 4.39 Hz), 8.42−8.41(d, 1H, J = 4.39 Hz), 8.32 (s, 1H), 8.241−8.162 (m, 10H), 7.91−7.75 (m, 10H), 2.76 (s, 3H), 2.69 (s, 3H), −0.72 (s, 1H) and at 223K 13.49 (s, 1H), 3.09 (s, 1H), 2.99 (s, 1H).

2-Aza-21-carba-23-oxa-5,10,15,20-tetraphenyl Porphyrin 6f. 2,5-Bis(phenyl hydroxy methyl) furan **5d** (0.3 g, 1.07 mmol) and **4b** (0.40 g, 1.07 mmol), *p*-toluene sulfonic acid (0.05 g, 0.27 mmol), and chloranil (0.39 g, 1.61 mmol) under similar reaction conditions explained above gave bluish green solid identified as **6f** on basic alumina column with ethyl acetate and dichloromethane (12:88) mixture as eluent. The bluish green lustrous solid was recrystallized in dichloromethane and *n*-hexane mixture (0.13 g, 19%), which decomposes above 300 °C. MS (electro spray) *m*/*z* (%): 616.2 (100) $[M]^+$. Anal. Calcd for $C_{44}H_{29}N_3O$: C 85.83, H 4.75, N 6.82. Found: C 85.63, H 4.59, N 6.62. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.74−8.72 (m, 2H), 8.69 (s, 1H), 8.53−8.52 (d, 1H, J = 4.5 Hz), 8.51−8.50 (d, 1H, J = 5 Hz), 8.29−8.28 (d, 1H, J = 7.5 Hz), 8.27−8.22 (d, 1H, J = 7 Hz), 8.12−8.09 (m, 6H), 7.79−7.71 (m, 14H), −2.55 (s, 1H).

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles and thermal parameters for compound **6b**, ^{1}H−^{1}H COSY for free base and diprotonated form, HMBC and HMQC correlation for diprotonated form at 298 K and NOESY spectrum at 223 K, UV−vis spectrum of freebase, monoprotonated and diprotonated form of **6c** and NMR chemical shift values. This material is available free of charge via the Internet at http://pubs.acs.org.

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