Inorganic Chemistry
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Pitfalls in Bromination Reactions of Zinc Porphyrins: Two-Sided Ring Opening of the Porphyrin Macrocycle

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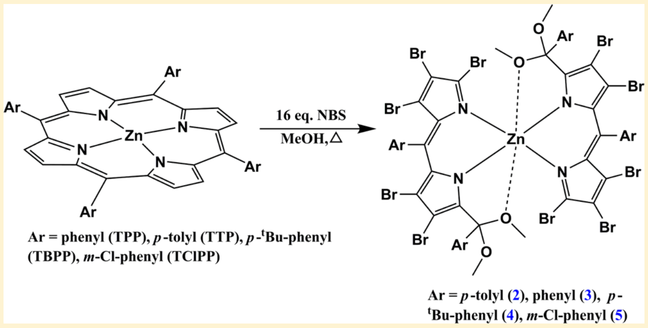
Ⓢ *Supporting Information*

ABSTRACT: Reaction of [Zn^{II}(TTP)] (**1**) (TTP = dianion of 5,10,15,20-*meso*-tetrakis(*p*-tolyl)porphyrin) with 16 equiv of *N*-bromosuccinamide (NBS) in methanol at reflux led to the unexpected two-sidedd open-ring brominated product [Zn^{II}($C_{26}H_{20}N_2O_2Br_5$)$_2$] (**2**). Similar observations have been made with other *meso*-substituted zinc porphyrins as well [Zn^{II}(por)] {por = dianion of 5,10,15,20-*meso*-tetrakis(aryl)-porphyrin; aryl = phenyl (TPP), *p*-^{t}Bu-phenyl (TBPP), *m*-Cl-phenyl (TClPP)}. The respective products [Zn^{II}($C_{24}H_{16}N_2O_2Br_5$)$_2$] (**3**), [Zn^{II}($C_{32}H_{32}N_2O_2Br_5$)$_2$] (**4**), and [Zn^{II}($C_{24}H_{14}N_2O_2Cl_2Br_5$)$_2$] (**5**) have been isolated in good to moderate yields and characterized by elemental analysis and UV−vis, ^{1}H NMR, and mass spectrometry. Additional bromination reaction of **1** with 8 equiv of NBS in a chloroform/methanol mixture led (after the two-sided ring opening) to nonmetalated brominated bi(pyrrole) product, $C_{36}H_{34}N_2O_4Br_4$ (**6**). The detailed structures of complexes **1**, **2**, **3**, and **6**, available in a single crystal form, have been confirmed by X-ray diffraction analysis.



■ INTRODUCTION

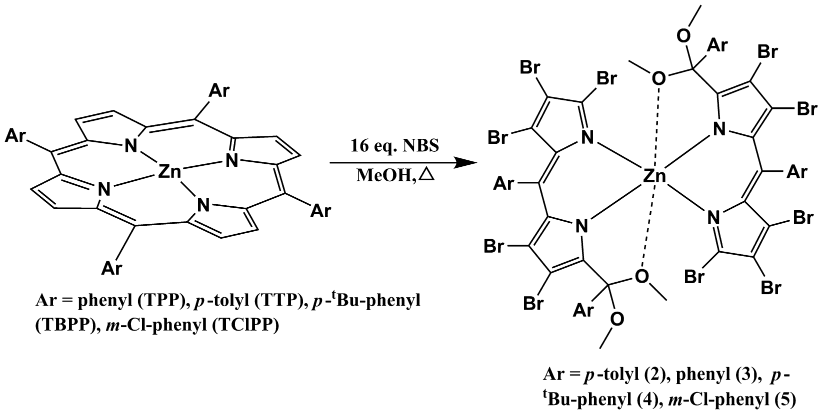
The synthesis of different kinds of bromine-substituted porphyrins or metalloporphyrins deserved a considerable attention over the years, because of their wide range of use in cross-coupling reactions.[1−4] These porphyrins have also been subjects of investigation for their electrochemical and optical[5] as well as antitumor[6] characteristics. They are also found to be involved in the construction of supramolecular and chiral architectures reported by our group.[7]

Several methodologies have been reported in the literature to synthesize the bromo-substituted porphyrins.[8] The *meso*-substituted bromo-porphyrins or metalloporphyrins are generally achieved by using NBS as the brominating agent.[9,1c,2a,3g,4e] Sometimes, *N*-bromoacetamide is also used instead of NBS.[3c] For bromination of *β*-pyrrolic positions, both molecular bromine and NBS are commonly applied; the latter has appeared to be the favorable and more convenient brominating reagent, as molecular bromine has substantial limitations.[10] Condensation of aldehyde with 3-bromo- or 3,4-dibromo-substituted pyrrole can also lead to the *β*-brominated porphyrins, but this methodology is generally avoided as it involves a tedious workup.[8a]

Our recent interest in the field of metalloporphyrin chemistry involves crystal engineering efforts to construct supramolecular porphyrin assemblies directed by halogen bonding interactions. We have shown that halogen atoms (−Br, −I), when placed either at the *meso*-substituted phenyl groups or on the axial ligands, readily take part in interactions with complementary electron-rich heterosubstituents (N, O) of neighboring porphyrin species, formulating halogen-bonded network architectures.[7b,11] At the next stage, this work was expanded to explore whether similar effects can be achieved with halogen atom(s) introduced at *β*-pyrrolic positions of the porphyrin macrocycle. Our initial intention was to synthesize the *β*-Br_8Zn(TTP) by using NBS as the brominating agent in methanol.[10c] Surprisingly, the reaction of [Zn(TTP)] (**1**) with NBS in methanol gave the unexpected two-sided ring-opening structure [Zn($C_{26}H_{20}Br_5N_2O_2$)$_2$] (**2**).[12] In nature, the degradation of plant pigment chlorophyll occurs by the loss of magnesium from the center of the macrocycle along with some structural changes in the macrocycle.[13] The animal pigment heme degradation leads to biliverdin, which is an open-chain tetrapyrrolic moiety, and the reaction is catalyzed by heme oxygenase.[14] The initial process of degradation involves the introduction of a hydroxyl group in one of its *meso* positions.[15] Balch et al. have studied in detail some model heme complexes in the context of the related natural heme-degradation process.[16] In the present study, we observe the two-sided ring opening of the Zn-porphyrins where the two bipyrrolic entities are held together through coordination to the central zinc ion in the final product(s) (Scheme 1). Further details of this interesting reaction are presented below, including spectroscopic and structural characterizations of the ring-opening products. To the best of our knowledge, such two-sided ring opening of metalloporphyrins has not been reported earlier.

Received: February 27, 2014
Published: July 16, 2014

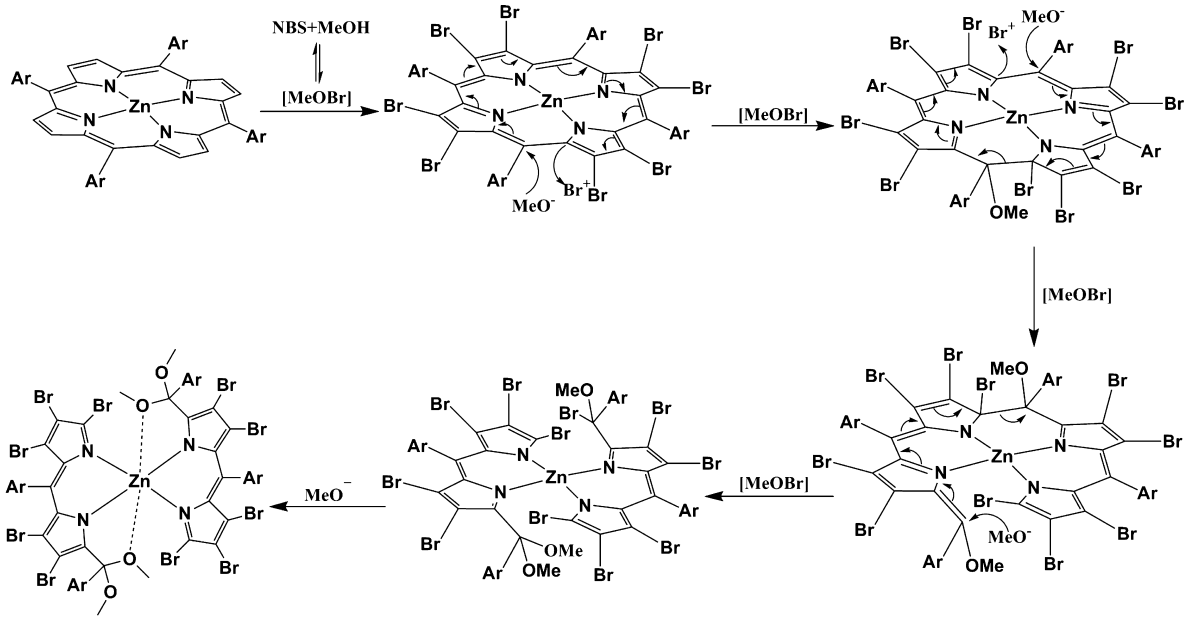
Scheme 1. Two-Sided Ring-Opening Reaction of [Zn(por)]



Ar = phenyl (TPP), *p*-tolyl (TTP), *p*-^{t}Bu-phenyl (TBPP), *m*-Cl-phenyl (TClPP)

Ar = *p*-tolyl (**2**), phenyl (**3**), *p*-^{t}Bu-phenyl (**4**), *m*-Cl-phenyl (**5**)

Scheme 2. Proposed Mechanism for Formation of the Open-Ring Product from the [Zn-Tetraarylporphyrins]



■ EXPERIMENTAL SECTION

Materials. Pyrrole, *p*-tolualdehyde, benzaldehyde, *p-tert*-butylbenzaldehyde, and *m*-chlorobenzaldehyde were obtained from Sigma-Aldrich. Solvents like propionic acid, chloroform, dichloromethane (DCM), methanol, and hexane were obtained from Bio-Lab Ltd., Israel. Petroleum ether (60−80 °C) was obtained from Frutarom Ltd., Israel. Zinc chloride, silica gel 60, and NBS were obtained from Merck. Free-base porphyrins were prepared following the method of Adler et al.[17]

Physical Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were obtained with a PerkinElmer 2400 microanalyzer. IR spectra were recorded on a Bruker Tensor 27 system spectrophotometer in ATR mode. Electronic absorption spectral measurements were carried out with an SP-1900 UV−vis spectrophotometer. Electron spray ionization mass spectrometry (ESI-MS) spectra were recorded on a SYNAPT spectrometer. The ESI-MS capillary was set at 3.5 kV, and the cone voltage was 10 V. The mass spectral peaks were composed of isotopic distribution, and only the central strong line is reported. ^{1}H NMR spectroscopic measurements of the complexes were recorded with a Bruker UltraShield 400 MHz NMR spectrometer.

The X-ray measurements (Bruker-ApexDuo diffractometer, MoKα Iμ microfocus X-ray source) were carried out at ca. 110(2) K on crystals coated with a thin layer of amorphous oil to minimize crystal deterioration, possible structural disorder, and related thermal motion effects and to optimize the precision of the structural results. These structures were solved by direct methods and refined by full-matrix least-squares (SIR-97, SHELXTL-2013 and SHELXL-97).[18,19] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in idealized/calculated positions and were refined using a riding model.

Synthesis. *Synthesis of 2.* A 14.6 mg (0.02 mmol) portion of **1** was taken in 15 mL of methanol in a 50 mL round-bottom flask. Then, 57 mg (0.32 mmol) of NBS was added to it and the solution was refluxed for 2 h. The solvent was evaporated in a rotary evaporator to give a pale red solid. The solid was dissolved in a minimum amount of $CHCl_3$/hexane (1:1) and passed through a column (20 × 3 cm) packed with Silica 60. The pinkish red solution was collected and evaporated to dryness to give a red solid. The solid was recrystallized from DCM and petroleum ether (60−80 °C) to give pink needle-shaped crystals. Yield: 72%. The synthesis of **1** is described in the Supporting Information.

Molecular formula $C_{52}H_{40}N_4O_4Br_{10}Zn$. Elem. Anal. Calcd (found) for $C_{52}H_{40}Br_{10}N_4O_4Zn$: C, 37.87 (37.52); H, 2.44 (2.46); N, 3.40 (3.44). UV−vis [CH_2Cl_2; λ_{max} (relative ε)]: 394 (15.50), 518 (100). ESI-MS (m/z): 1647.38 ([M]$^+$); ^{1}H NMR ($CDCl_3$): δ 2.85 (12H, s), 2.39 (12H, s); aromatic protons signals are overlapped between δ 6.8−7.3.

Syntheses of 3, 4, and 5. Syntheses of these complexes were made by following a similar methodology as that described for **2**, using

[Zn(TPP)], [Zn(TBPP)], and [Zn(TClPP)], respectively, instead of [Zn(TTP)] by taking the starting materials in a similar stoichiometric ratio. The corresponding yields are 73, 53, and 64%. In all cases, the ring-opening reactions are associated with a sharp color change from the deep purple color of the zinc porphyrin reactant to a pink color of the products **2**–**5**.

Data for **3**: Molecular formula $C_{48}H_{32}N_4O_4Br_{10}Zn$. Elem. Anal. Calcd (found) for $C_{48}H_{32}N_4O_4Br_{10}Zn$: C, 36.18 (36.41); H, 2.02 (2.09); N, 3.52 (3.64). UV–vis [CH_2Cl_2; λ_{max} (relative ε)]: 382 (10.87), 520 (100). ESI-MS (m/z): 1593.40 ($[M]^+$).

Data for **4**: Molecular formula $C_{64}H_{64}N_4O_4Br_{10}Zn$. Elem. Anal. Calcd (found) for $C_{64}H_{64}N_4O_4Br_{10}Zn$: C, 42.29 (42.31); H, 3.55 (3.61); N, 3.08 (3.04). UV–vis [CH_2Cl_2; λ_{max} (relative ε)]: 396 (13.15), 520 (100). ESI-MS (m/z): 1817.65 ($[M]^+$).

Data for **5**: Molecular formula $C_{48}H_{28}N_4O_4Cl_4Br_{10}Zn$. Elem. Anal. Calcd (found) for $C_{48}H_{28}N_4O_4Cl_4Br_{10}Zn$: C, 33.30 (33.31); H, 1.63 (1.68); N, 3.24 (3.28). UV–vis [CH_2Cl_2; λ_{max} (relative ε)]: 392 (11.23), 520 (100). ESI-MS (m/z): 1731.20 ($[M]^+$).

■ RESULTS AND DISCUSSION

Synthesis. The reaction of [Zn(TTP)] (**1**) with 16 equiv of NBS in methanol at reflux yielded a pink/red solution. TLC of the crude solution shows the complete loss of **1** and only one colored (pink) band, suggesting exclusive formation of a new compound. Subsequent work up, followed by crystallization from DCM/hexane solution, gave needle-shaped crystals of **2**. Similar observations have also been made with different *meso*-substituted zinc porphyrins [Zn(TPP)], [Zn(TBPP)], and [Zn(TClBP)], and the respective products **3**, **4**, and **5** have been isolated in good to moderate yields. It has been reported that Br atoms at the β-pyrrolic positions have a profound influence on the redox potentials and cause a severe distortion of the porphyrins from a flat conformation to a saddle-shaped conformation.[10a,e,20] In the present case, however, the [Zn(por)] after bromination at eight β-pyrrolic positions overcomes the steric repulsions by ring opening at two opposite *meso* positions in the presence of excess MeOBr.[21]

The nucleophilic attack by the methoxide ion at the *meso* position, followed by electrophilic substitution at the α-position of the pyrrols by bromine, leads to the formation of two sp^3-carbon atoms with the loss of aromaticity as well as destruction of the porphyrin macrocycle (Scheme 1). The proposed mechanism for such a process is shown in Scheme 2. The use of more NBS up to 32 equiv and prolonged reflux (around 6 h) did not lead to further destruction of the molecules (no electronic spectral change), suggesting that the incorporation of additional bromine to the products is difficult in this type of ring-opening reaction.

A similar two-sided ring-opening product is also formed when the reaction(s) is performed under an Ar atmosphere (i.e., in the absence of oxygen), indicating that oxygen is not involved in the ring-opening process, in contrast to the Fe-OEP complex.[16] The reaction was also unaffected when ethanol is used as the solvent instead of methanol, likewise when the solvent is a 10:1 MeOH:pyridine. Total destruction of the zinc porphyrin is observed when excess Br_2 is used as brominating agent in methanol (or in CCl_4)[8a,10g] at reflux, yielding a colorless solution. Supplementary information and further support of the proposed mechanism were obtained when the bromination reaction of **1** was carried out in a $CHCl_3$/MeOH (2:1) mixture, using 8 equiv of NBS. The room-temperature stirring of solution containing the reactants for 2 h led to the bromination at the β-pyrrolic positions as well as ring breaking at the *meso* positions. This reaction was accompanied, however, by demetalation of the pyrrolic compound.[22] Similar results were obtained in a 10:1 $CHCl_3$/MeOH mixture, but in such conditions, the ring-breaking reaction takes longer (12 h), most probably due to poor solubility of NBS in chloroform. The isolation and structural characterization of this brominated bipyrrolic derivative, $C_{36}H_{34}N_2O_4Br_4$ (**6**), is in line with the assumed nucleophilic attack of the methoxide ion at the *meso* position after octabromination of the zinc porphyrins (Scheme 2). The molecular structure of **6** is shown below.

Crystal Structures. The starting material (**1**), as well as products **2**, **3**, and **6** available in crystalline form (single crystals obtained by slow evaporation of DCM/petroleum ether solution of the corresponding product), have been structurally characterized by single-crystal X-ray diffraction analysis. Compounds **2** and **3** crystallized as DCM solvates. Crystals of **3** were of somewhat lower quality due solvent disorder therein, which affected the precision of the crystallographic determination. No crystals of **4** and **5** suitable for X-ray diffraction analysis could be obtained. The crystallographic data for **1**–**3** and **6** are as follows:

1: $C_{48}H_{36}N_4Zn$, M = 734.18, monoclinic, space group $P2_1/n$, a = 9.5745(5) Å, b = 9.2610(5) Å, c = 21.0029(11) Å, β = 99.734(2)°, V = 1835.5(2) Å^3, Z = 2, T = 110(2) K, D_c = 1.328 Mg/m^3, μ = 0.71 mm^{-1}. 17 498 reflections measured, of which 4570 were unique (R_{int} = 0.037) and 3717 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 56.6°. Final R1 = 0.037 and wR2 = 0.092 for the 3717 data above the intensity threshold, and R1 = 0.051 and wR2 = 0.099 for all data. CCDC 988944. Structure description of **1** is given in the Supporting Information.

2: $2(C_{52}H_{40}Br_{10}N_4O_4Zn)\cdot 3(CH_2Cl_2)$, M = 3553.48, monoclinic, space group $P2_1/n$, a = 16.8255(5) Å, b = 18.3237(5) Å, c = 19.8035(6) Å, β = 95.885(1)°, V = 6073.3(3) Å^3, Z = 2, T = 110(2) K, D_c = 1.943 Mg/m^3, μ = 7.16 mm^{-1}. 42 426 reflections measured, of which 10754 were unique (R_{int} = 0.031) and 8886 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 50.2°. Final R1 = 0.029 and wR2 = 0.073 for the 8886 data above the intensity threshold, and R1 = 0.041 and wR2 = 0.078 for all data. CCDC 988945.

3: $2(C_{48}H_{32}Br_{10}N_4O_4Zn)\cdot(1 + x)(CH_2Cl_2)$, M = 3271.31, monoclinic, space group $P2_1/c$, a = 22.0103(9) Å, b = 21.6959(8) Å, c = 22.7148(8) Å, β = 90.858(1)°, V = 10845.9(7) Å^3, Z = 4, T = 110(2) K, D_c = 2.003 Mg/m^3, μ = 7.92 mm^{-1} (excluding the unknown fraction x of the DCM crystallization solvent). 74 009 reflections measured, of which 19 900 were unique (R_{int} = 0.089) and 13 163 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 50.8°. Final R1 = 0.082 and wR2 = 0.168 for the 13 163 data above the intensity threshold, and R1 = 0.135 and wR2 = 0.186 for all data. CCDC 988946.

6: $C_{36}H_{34}Br_4N_2O_4$, M = 878.29, tetragonal, space group $I\bar{4}2d$, a = 26.8013(11) Å, b = 26.8013(11) Å, c = 9.6943(4) Å, V = 6963.5(5) Å^3, Z = 8, T = 110(2) K, D_c = 1.676 Mg/m^3, μ = 4.66 mm^{-1}. 11 846 reflections measured, of which 3073 were unique (R_{int} = 0.043) and 2632 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 50.1°. Final R1 = 0.027 and wR2 = 0.057 for the 2632 data above the intensity threshold, and R1 = 0.041 and wR2 = 0.062 for all data. CCDC 988947.

The molecular structure of product **2** is illustrated in Figure 1. The asymmetric unit contains one molecule of **2** and $1^1/_2$ solvent DCM species. The crystallographic analysis reveals that a total of 10 bromine atoms have been incorporated into the molecule. Two *trans*-related *meso* positions of the porphyrin ring open up and form sp^3-carbon sites bearing one tolyl group and two methoxy substituents. All the β-pyrrolic positions and

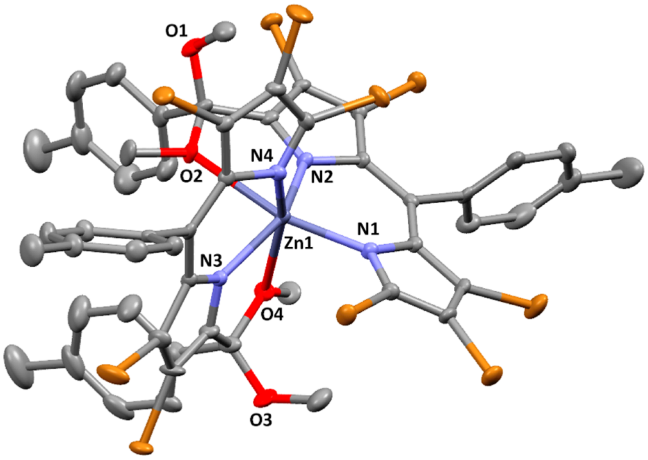


Figure 1. Molecular structure of **2** with 50% probability atomic displacement parameters (hydrogen atoms and DCM solvent are omitted for clarity; only the major position of the partly disordered Br7 is shown). Selected bond distances (Å): Zn1−N1 = 2.041(3), Zn1−N2 = 1.989(3), Zn1−N3 = 1.998(3), Zn1−N4 = 2.050(3). Note that O2 and O4 lie also in close proximity to Zn1, providing along with the four N atoms a pseudo-octahedral coordination environment.

one α-position from each fragment are substituted now by bromine atoms. The central zinc ion is strongly coordinated to the four N(pyrrole) atoms at Zn−N bond distances in the range of 1.989−2.050(3) Å, and weakly interacting also with two of the methoxy O atoms, O2 and O4, at 2.536(3) and 2.501(3) Å, respectively. The zinc ion thus adopts a distorted tetrahedral geometry with respect to the coordinated N-sites, and a distorted octahedral geometry when the two O-sites (occupying *cis*-related coordination sites) are taken into consideration as well.

Similar results were obtained when the bromination reaction was repeated with the closely related [Zn(por)] complex. The molecular structure of the product **3** is depicted in Figure 2. The asymmetric unit of this crystal structure consists of two molecules of the zinc complex and two DCM solvent moieties, one well ordered and the other severely disordered in the crystal lattice. As in the previous case, the $C_{48}H_{32}N_4O_4Br_{10}Zn$ product reveals the two-sided ring opening of the porphyrin macrocycle, associated with substitution of 10 Br atoms on the molecular framework. The two crystallographically independent molecules, while differing slightly in their conformational features, exhibit similar distorted octahedral coordination geometries around the central zinc ions, and the corresponding Zn−N and Zn···O distances within the zinc-coordination spheres are within 1.983(9)−2.064(9) Å and 2.463(7)−2.488(8) Å in one molecule and 1.993(9)−2.070(9) Å and 2.502(7)−2.545(7) Å in the other species.

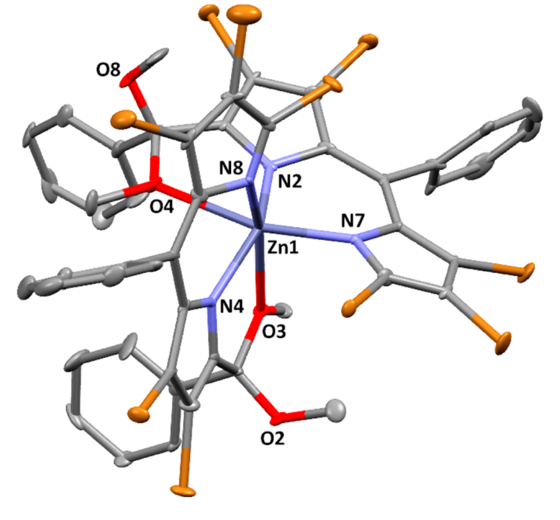


Figure 2. Perspective view of one of the molecules in **3** with 50% probability atomic displacement parameters/ellipsoids (hydrogen atoms and DCM solvent are omitted for clarity). Note the close overall resemblance of the molecular structure of **3** to that of **2** shown in Figure 1.

The molecular structure of the ring-opening product **6** is illustrated in Figure 3. The structural analysis revealed that the β-pyrrolic positions are occupied by the bromine atoms and the α-carbons are bonded to sp^3-carbon atoms that are having two methoxy groups and one tolyl group to complete the tetrahedral geometry. The different stoichiometric ratio of the porphyrin and NBS reactants (along with the modified experimental conditions), with respect to the previous experiments, resulted in slightly different patterns of the Br-substitution (limited this time to the β-carbons only) and methoxy-driven (asymmetric) two-sided ring opening of the porphyrin macrocycle.

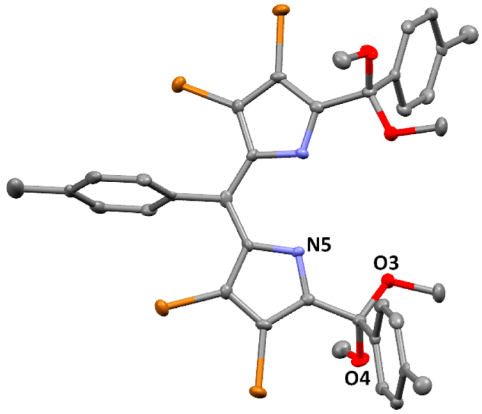


Figure 3. Ball-and-stick illustration of the molecular structure of **6** with 50% probability atomic displacement parameters, which resides in the crystal on axes of 2-fold rotation (hydrogen atoms are omitted for clarity).

Spectroscopy. The course of the reaction (**1** to **2**) was monitored by the UV−vis spectral studies, which showed that the reaction between **1** and NBS occurs very rapidly in the present reaction conditions with the complete disappearance of the Soret band of **1** within 5 min. A strong absorption band appears at 480 nm, which then splits into two bands at 470 nm and another at a slightly higher wavelength. The band at 470 nm is indicative of the β-$Br_8Zn(TTP)$, which shows a Soret band at 469 nm in DCM.[20] The band appearing initially at 480 nm may be composed of the β-$Br_8Zn(TTP)$ and any of the intermediates (shown in Scheme 2). During the reaction, the higher wavelength band starts to increase in intensity with the shifting of its position, ending eventually as a strong peak at 519 nm for the formation of the final product **2** (Figure 4a).

A comparison of UV−visible spectra of **1** and **2** in the region of 300−800 nm in DCM is shown in Figure 4b. The disappearance of the Q-band (in **2**) at the expected region (580−660 nm) for octabrominated metalloporphyrins[20] and

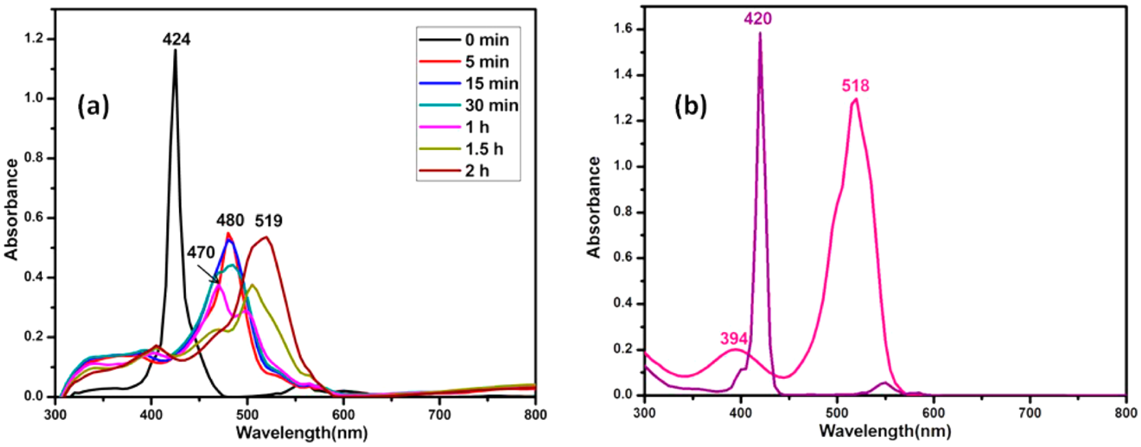


Figure 4. (a) The electronic spectral changes in the transformation of **1** (1.1×10^{-5} M) to **2** in MeOH. The band at 470 nm is indicative of the initial formation of β-Br_8Zn(TTP) (see Results and Discussion). (b) Comparison of electronic spectra of **1** (1.2×10^{-5} M, purple) and purified **2** (2.3×10^{-4} M, pink) in DCM.

the appearance of a strong band at higher wavelength (518−519 nm) similar to BODIPY derivatives[23] are consistent with the two-sided porphyrin ring opening. Similar spectral features are also observed for **3**, **4**, and **5** (see Figures S2−S4 in the Supporting Information).

^{1}H NMR spectra of **1** and **2** in the range of δ 6−10 are displayed in Figure 5. The spectrum of **2** revealed a nonaromatic conjugated system. The signal for the β-pyrrolic protons was absent as compared to **1**, which shows a sharp peak at δ 8.89 for eight protons, suggesting that those positions are occupied by the bromine atoms in **2**. The signals for the *ortho* and *meta* positions give overlapping signals in the range of δ 6.8−7.3 for **2** compared to sharp signals in case of **1**, as shown in Figure 5. (see also Figures S8−S12 in the Supporting Information). Monitoring of the reaction in CD_3OD by ^{1}HNMR spectroscopic analysis shows the disappearance of the signal for pyrrolic protons within 5 min after addition of NBS, indicating the generation of β-Br_8Zn(TTP) in the solution. The signal for other aromatic protons becomes broader. With time, the signal for methoxy protons starts to generate at δ 2.3−2.5 ppm, and eventually it splits (see Figure S7 in the Supporting Information).

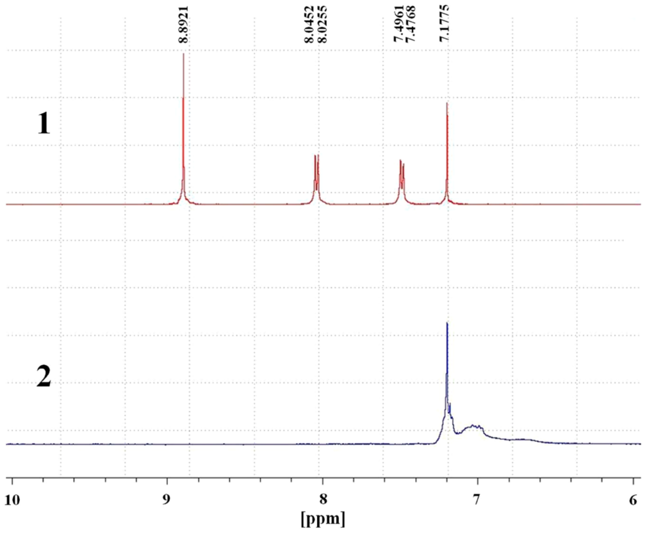


Figure 5. Comparison of ^{1}H NMR (400 MHz) spectra of **1** and **2** in $CDCl_3$.

In the ESI-MS spectrum of the complexes in DCM, the molecular ion peak (m/Z) could be observed as an intense peak (see in the Supporting Information) with excellent isotopic distribution. However, in **2**, **3**, **4**, and **5**, the peak corresponding to the m/Z value with the loss of one methoxy group has higher intensity than the molecular ion peak. ESI-MS spectra for compounds **1**−**5** are shown, respectively, in Figures S13−S17 in the Supporting Information.

■ CONCLUSION

An unusual observation has been made in attempts to octabrominate the zinc porphyrins using NBS in methanol at reflux. The bromination reactions were associated with the two-sided ring opening of the metalloporphyrin ring, leading to unexpected products **2**−**5**. No further degradation has been observed under harsher conditions. The structures of complexes **2** and **3** have been confirmed unequivocally by single-crystal X-ray diffraction analysis. The observed results strongly suggest that the methanol should be avoided in bromination reactions of Zn-porphyrins using NBS as the brominating agent. While single ring opening of the tetraarylporphyrin macrocycle in alcoholic environments has been observed recently,[12] the two-sided opening is being reported here for the first time. The present findings may provide additional insight into the degradation of natural pigments like chlorophyll and hemoglobin, which dominate the plant and animal kingdom, respectively. The generality of this phenomenon is currently being probed with other metalloporphyrin systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and solid-state structure of **1**; UV−vis, FT-IR, ^{1}H NMR, and ESI-MS spectra; and X-ray crystallographic data (in CIF format; CCDC 988944−988947). This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding

This research was supported by the Israel Science Foundation − Grant No. 108/12.

Notes

The authors declare no competing financial interest.

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