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Synthesis and Characterization of 4-Chlorobutyl Ester of 5-(8-Carboxyl-1-naphthyl)-10,15,20-triphenyl-porphyrin and its Zinc Complex

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In the presence of Brønsted–Lowry acids (phenol or dry HCl), the acyl chloride, which was obtained by the reaction between 5-(8-carboxyl-1-naphthyl) -10,15,20-triphenyl-porphyrin (CNTPP) and oxalyl chloride, reacted with tetrahydrofuran and led to the 4-chlorobutyl ester, **P1**, as the result of the acylative cleavage. **P1** and its zinc complex **[ZnP1]** have been characterized by ^{1}H NMR. The structure of **[ZnP1]** was obtained by X-ray crystallography. Zinc is coordinated by four pyrrole nitrogens. The 8-position substituent, a 4-chlorobutyl ester group, lies above the porphyrin plane.

Keywords

chlorobutyl; porphyrin; acylative cleavage; tetrahydrofuran; acid.

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1. Introduction

Porphyrins and their derivatives have been found in many biological systems, such as hemoglobin, cytochrome P450, horseradish peroxidase, etc. Besides their importance in biological sciences, porphyrins have also play important roles in material sciences, such as catalytic asymmetric synthesis, nonlinear optics, molecular devices, etc.[1-5] One attracting feature of the porphyrin species is that it can be functionalized at many positions, such as *meso* or β positions, which can lead to many kind of novel porphyrins with various structures and functions.

We have recently been working on a series of mononaphthyl substituted porphyrins.[6-11] These porphyrins can be easily functionalized at the 8-position of the naphthyl group. For example, we have designed and synthesized its phenolate derivative with a covalently attached phenol tail, the ligand **P3** (shown in Scheme 1), as a structural mimic of catalases, which has a hanged phenol group at the appropriate position to further interact with the center metal.[8] In that preparation, dichloromethane was used as the solvent. When we extended it to other phenols, we tried to use tetrahydrofuran (THF) as the solvent. Interestingly, the 4-chlorobutyl ester, **P1**, has been obtained as the major product as shown in Scheme 1. Its zinc complex was also prepared and crystallographically characterized. Herein, we report the synthesis and characterization of **P1** and **[ZnP1]**.

2. Experimental Section

2.1. *General procedures*

2.1.1. Materials and General Methods. All reagents were obtained from commercial sources without further purification unless otherwise noted. Anhydrous tetrahydrofuran (THF) was dried and redistilled over sodium benzophenone ketyl. The dichloromethane (CH_2Cl_2) was freshly distilled from CaH_2 under nitrogen used. CNTPP was synthesized according to the reported method.[10] ^1H NMR spectra were carried out using a Bruker AVANCE 400 spectrometer in $CDCl_3$. Mass spectra were taken with Agilent 6220 Accurate-Mass TOF LC/MS. UV-vis spectra were measured with a Shimadzu UV-3150 spectrometer. IR spectra were measured with a Bruker vertex-70 spectrometer. The single crystal structure was measured with Agilent Xcalibur diffractometer with an Atlas (Gemini Ultra Cu) detector. Elemental analyses (C, H and N) were performed with an Elementar Vario EL III analytical instrument.

2.2. Synthesis

2.2.1. Synthesis of *compound P1, P2, P3, P4, P5*

5-(8-carboxyl-1-naphthyl)-10, 15, 20-triphenyl-porphyrinate (CNTPP) (0.20 g, 0.28 mmol) was dissolved in dichloromethane (20 mL). Oxalyl chloride (4.0 mL, 42 mmol) was slowly added to the above solution and stirred for 2 h under N_2. The excess reagent was removed under reduced pressure. The residue was redissolved in anhydrous THF. The corresponding phenol (phenol for **P2**, catechol for **P3**, *m*-dihydroxybenzene for **P4**, hydroquinone for **P5**, 60 equiv.)

was added to the solution and stirred for 16 h. The solution was rotor evaporated to dryness under vacuum. The red solid was purified by silicon chromatography, eluted with CH_2Cl_2/petroleum ether (1:1). For phenol, **P1**, yield 69%; **P2**, yield 16%. For catechol, **P1**, yield 82%; **P3**, yield 12%. For *m*-dihydroxybenzene, **P1**, yield 76%, **P4**, yield 15%**.** For hydroquinone, **P1**, yield 73%; **P5**, yield 14%.

P1, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 4H), 8.77 (d, 2H), 8.63 (d, 2H), 8.33 (t, 4H), 8.25 (t, 3H), 8.10 (d, 2H), 7.90 (t, 1H), 7.76 (m, 9H), 7.56 (t, 1H), 7.32 (d, 1H), 2.16 (t, 2H), 0.33 (s, 2H), -0.08 (s, 2H), -0.58 (m, 2H), -2.67 (s, 2H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$): 421 (5.45×10^5), 518 (2.17×10^4), 553 (8.67×10^3), 592 (6.55×10^3), 649 (3.84×10^3). IR(KBr): *v*,cm^{-1} 3431 (m), 3316 (m), 3053 (m), 2953 (m), 1716 (s), 1596 (m), 1558 (m), 1473 (s), 1440 (m), 1363 (s), 1347 (s), 1194 (s), 1175 (m), 973 (s), 801 (s), 775 (s), 730 (s), 515 (w). LC-ESI-MS: m/z calcd for $C_{53}H_{39}ClN_4O_2$ 798.28; found 799.28 $[M+H]^+$. Anal. Calc. $C_{53}H_{39}ClN_4O_2\cdot 2.0CH_2Cl_2$: C, 68.16; H, 4.47; N, 5.78%. Found: C, 68.45; H, 4.36; N, 5.89%.

P2, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, 2H), 8.81 (d, 2H), 8.69 (d, 2H), 8.66 (s, 2H), 8.48 (d, 1H), 8.33 (m , 4H), 8.12 (d, 4H), 7.95 (t, 1H), 7.80 (s, 3H), 7.72 (m, 6H), 7.61 (m, 2H), 5.61 (t, 1H), 4.77 (t, 2H), 3.67 (d, 2H), -2.60 (s, 2H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$): 423 (5.45×10^5), 519 (2.24×10^4), 555 (9.61×10^3), 594 (6.82×10^3), 649(3.95×10^3). IR(KBr): *v*,cm^{-1} 3312 (m), 3052 (m), 1739 (s), 1594 (m), 1558 (m), 1490 (s), 1473 (m), 1440 (m), 1184 (s), 963 (s), 801 (s), 729 (s), 699 (s). LC-ESI-MS: m/z calcd for $C_{55}H_{36}N_4O_2$ 784.28; found 807.27

$[M+Na]^+$. Anal. Calc. $C_{55}H_{36}N_4O_2 \cdot 1.0CH_2Cl_2$: C, 77.33; H, 4.40; N, 6.44%. Found: C, 78.97; H, 4.36; N, 6.55%.

P3, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, 2H), 8.78 (d, 2H), 8.68 (d, 2H), 8.61 (d, 2H), 8.46 (d, 1H), 8.36 (d, 1H), 8.33 (d, 1H), 8.25 (d, 2H), 8.16 (d, 2H), 8.09 (d, 2H), 7.96 (t, 1H), 7.79 (s, 3H), 7.72 (m, 6H), 7.62 (t, 1H), 7.55 (d, 1H), 5.43 (m, 2H), 3.41 (t, 1H), 2.54 (d, 1H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1} \cdot cm^{-1}$): 422 (5.51×10^5), 519 (2.14×10^4), 555 (1.00×10^3), 594 (6.34×10^3), 649 (3.62×10^3). IR(KBr): *v*,cm^{-1} 3416 (m), 3314 (m), 3051 (m), 2952 (m), 1740 (m), 1596 (m), 1492 (m), 1472 (m), 1459 (m), 1440 (m), 1265 (s), 1174 (s), 964 (s), 800 (s), 729 (s), 700 (s), 558 (w). LC-ESI-MS: m/z calcd for $C_{55}H_{36}N_4O_3$ 800.28; found 801.29 $[M+H]^+$. Anal. Calcd for $C_{55}H_{36}N_4O_3 \cdot 0.7CH_2Cl_2$: C, 77.76; H, 4.38; N, 6.51. Found: C, 77.54; H, 4.36; N, 6.48.

P4, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, 2H), 8.86 (d, 2H), 8.73 (d, 2H), 8.66 (s, 2H), 8.57 (d, 1H), 8.37 (m , 1H), 8.29 (m, 3H), 8.17 (d, 2H), 8.12 (d, 2H), 7.98 (t, 1H), 7.80 (s, 3H), 7.72 (m, 6H), 7.61 (t, 1H), 7.54 (d, 1H), 5.92 (t, 1H) , 5.19 (d, 1H), 5.07 (d, 1H), 0.06 (s, 1H), -0.56 (s, 1H) , -2.68. (s, 2H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1} \cdot cm^{-1}$): 423 (3.94×10^5), 519 (1.32×10^4), 555 (4.18×10^4), 594 (3.12×10^3), 649 (2.62×10^3). IR(KBr): *v*,cm^{-1} 3317 (m), 3052 (m), 2921 (m), 1739 (m), 1595 (m), 1473 (m), 1440 (m), 1347 (m), 1263 (m), 1184 (s), 1139 (s), 964 (m), 799 (s), 729 (s), 701 (s), 661 (w). LC-ESI-MS: m/z calcd for $C_{55}H_{36}N_4O_3$ 800.28; found 823.27 $[M+Na]^+$. Anal. Calc. $C_{55}H_{36}N_4O_3 \cdot 0.4CH_2Cl_2$: C, 79.70; H, 4.44; N, 6.71%. Found: C, 79.95; H, 4.32; N, 6.69%.

P5, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, 2H), 8.79 (d, 2H), 8.66 (d, 2H), 8.61 (s, 2H), 8.44 (d, 1H), 8.35 (m , 2H), 8.24 (s, 2H), 8.11 (m, 4H), 7.94 (t, 1H), 7.72 (m, 9H), 7.61 (t, 1H), 7.54 (d, 1H), 3.86 (d, 2H), 3.34 (t, 3H), -2.69 (s, 2H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$): 423 (4.06×10^5), 519 (1.67×10^4), 555 (7.39×10^3), 594 (5.17×10^3), 649 (3.5×10^3). IR(KBr): *v*,cm^{-1} 3385 (m), 3315 (m), 3051 (m), 2921 (m), 1737 (m), 1707 (m), 1596 (m), 1503 (s), 1472 (m), 1439 (m), 1347 (m), 1264 (m), 1175 (s), 1137 (m), 970 (m), 799 (s), 729 (s), 700 (s), 519 (w). LC-ESI-MS: m/z calcd for $C_{55}H_{36}N_4O_3$ 800.28; found 823.27 $[M+Na]^+$. Anal. Calc. $C_{55}H_{36}N_4O_3\cdot 0.4CH_2Cl_2$: C, 79.70; H, 4.44; N, 6.71%. Found: C, 79.84; H, 4.39; N, 6.59%.

2.2.2. Synthesis of compound *B1, B2*

Benzoyl chloride (110 μL, 0.91 mmol) was dissolved in anhydrous THF (30 mL) in Schlenk flask, and catechol (2.0 g, 18 mmol，20 equiv.) was added under N_2. After 48 h, the reaction was complete. The excess THF was rotor evaporated to dryness under vacuum. The light yellow liquid **B1** and **B2** obtained by chromatography (silica, CH_2Cl_2/petroleum ether 1 : 4).

For **B1**, yield (0.14 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 2H), 7.57 (t, 1H), 7.45 (t, 2H), 4.37 (t, 2H), 3.62 (t, 2H), 1.95 (m , 4H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$): 234 (1.1×10^4). IR(KBr): *v*,cm^{-1} 3421 (m), 2959 (s), 1719 (s), 1601 (w), 1451 (s), 1314 (s), 1274 (s), 1176 (m), 1115 (s), 1070 (s), 1026 (m), 711 (s). LC-ESI-MS:m/z calcd for $C_{11}H_{13}ClO_2$ 212.06; found 235.05 $[M+Na]^+$. Anal. Calc. $C_{11}H_{13}ClO_2\cdot 0.5H_2O$: C, 59.60; H, 6.37%. Found: C, 60.10; H, 6.41%.

For **B2**, yield (0.026 g, 13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, 2H), 7.67 (t, 1H), 7.54 (t, 2H), 7.18 (t, 2H), 7.07 (d, 1H), 6.98 (t , 1H), 5.62 (s, 1H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$): 234 (1.7×10^4). IR(KBr): *ν*,cm^{-1} 3412 (s), 1716 (s), 1614 (m), 1596 (s), 1511 (s), 1460 (s), 1346 (s), 1297 (s), 1272 (s), 1229 (s), 1175 (s), 1098 (s), 1068 (s), 753 (s), 712 (s), 557 (w). LC-ESI-MS: m/z calcd for $C_{13}H_{10}O_3$ 214.06; found 237.05 $[M+Na]^+$. Anal. Calc. $C_{13}H_{10}O_3\cdot 0.1H_2O$: C, 72.28; H, 4.76%. Found: C, 71.81; H, 4.53%.

2.2.3. Synthesis of compound B1 or P1 by using dry HCl.

Similar to the previous reactions, instead of phenol, dry HCl gas was passed through the solution for 10 mins. For **P1**, yield 91%; For **B1**, yield 93%.

2.2.4. Synthesis of [ZnP1]

A solution of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.125 g, 0.57 mmol) in methanol (5 mL) was added to the solution of **P1** (0.22 g, 0.28 mmol) in chloroform (50 mL). The mixture was refluxed for three hours. After the completion of the reaction, the solution was washed with water (3×100 mL). The organic layer was collected, then dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by chromatography (silica, CH_2Cl_2/hexane 1:1). The light purple solid was obtained. Yield 0.20 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (t, 4H), 8.85 (d, 2H), 8.70 (d, 2H), 8.29 (m, 7H) , 8.12 (d , 2H), 7.90 (t, 1H), 7.76 (m, 9H), 7.56 (t, 1H), 7.28 (d, 1H), 2.66 (t, 2H), 0.64 (t, 2H), 0.52 (m, 2H), 0.10 (m, 2H). UV-Vis (CH_2Cl_2): λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$): 423 (6.39×10^5), 551 (2.55×10^4), 592 (4.64×10^3). IR(KBr): *ν*,cm^{-1} 3420 (m), 3052

(m), 2951 (m), 1718 (s), 1595 (m), 1485 (m), 1439 (m), 1338 (s), 1205 (s), 1067 (m), 1003 (s),798 (s), 700 (s), 664 (w). LC-ESI-MS: m/z calcd for $ZnC_{53}H_{37}ClN_4O_2$ 860.19; found 861.20 $[M+H]^+$. Anal. Calc. $C_{53}H_{39}ClN_4O_2 \cdot 0.5CH_2Cl_2$: C, 70.99; H, 4.23; N, 6.19%. Found: C, 71.29; H, 4.35; N, 6.28%.

2.3. X-ray crystallography

Single crystals of **[ZnP1]** were obtained by slow evaporation of its solution in the mixture of dichloromethane and hexane (1:1). All measurements were made on Agilent Xcalibur diffractometer with an Atlas (Gemini Ultra Cu) detector by using graphite monochromated Cu Ka (λ = 0.154178 nm). A purple crystal with the dimensions 0.35 x 0.30 x 0.20 mm^3 was used for the structure determination. It was glued to a glass fiber by epoxy cement and measured at 223 K. Cell refinement and data reduction were carried out with the use of the program CrysAlisPro (Agilent Technologies, Version 1.171.36.32, 2013), and absorption corrections (multi-scan) were applied. The structure was solved by direct methods using SHELXS-97 and refined against F^2 using SHELXL-97;[12] subsequent difference Fourier syntheses led to the location of the remaining nonhydrogen atoms. For the structure refinement all data were used including negative intensities. The asymmetric unit contains one porphyrin molecule and one methylene chloride solvate. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added with the standard SHELXL-97 idealization methods. Brief crystal data for the structure are listed in Table 1.

3. Results and Discussion

The compound **P1** has been synthesized in anaerobic condition, the overall procedure is summarized in Scheme 1. Our original design is to synthesize **P2-P5**. Unexpectedly, the reaction led directly to the production of **P1**, a 4-chlorobutyl ester, as the major product; **P2 (**or **P3, P4, P5)** as the minor product. Their formulae have been confirmed by electrospary-ionization (ESI) mass spectrometry (shown in the supporting information). For example, ESI revealed the ion peaks at m/z = 799.28 for the compound **P1**, which corresponds to $[M+H]^+$.

In the reaction shown in Scheme 1, the butyl group was obviously from THF, the product **P1** was formed by the cleavage of tetrahydrofuran. The cleavage of THF with acyl chlorides is a useful reaction, particularly in the synthesis of molecules where a four-carbon chain is required to be added.[13-15] Besides the acyl chloride, phenol is the other possible reagent involving in the reaction. So phenol, a Brønsted–Lowry acid, could be the key reagent to promote the cleavage. We also tried to add NEt_3 during the reaction, no **P1** was obtained under such condition. It confirms the acidity of phenol is essential to the acylative cleavage of tetrahydrofuran. Since phenols are weak Brønsted–Lowry acids, how about strong Brønsted–Lowry acid? We also tried to use dry HCl as shown in Scheme 2. The reaction led to a higher yield of **P1** (91%). Furthermore, comparison experiments have been performed to benzoic chloride instead of CNTPP. As shown in Scheme 2, in the presence of excess catechol, the reaction ii led to both **B1** (4-chlorobutyl ester) and **B2**. When dry HCl was used, the reaction iii gave **B1** as the only

product. The above study suggests such acylative cleavage reaction is Brønsted–Lowry acid-promoted.

As we also learned from literatures that many catalysts have been reported for similar transformation. There are metallic complexes, such as $ZnCl_{2,}$[16] $FeCl_{3,}$[17] $MoCl_{5,}$[18] $InBr_{3,}$ [19] $BiCl_3$[20] and $La(NO_3)_{3,}$[21] or metals, such as Al,[22] Zn[23] and Mg,[24] or nonmetals, such as iodine[25] and graphite.[26] In most cases, they are Lewis acids. So it may not be too surprising in light of the results from analogous reactions using Brønsted–Lowry acids. The detailed reaction mechanism is not clear so far. It is likely that a tetrahydrofuran molecule is broken down, and subsequently forms a chlorobutyl ester with the 8-carboxyl-naphthyl group since it is known that THF is unstable under acidic condition, and can react with HCl to produce 4-chlorobutanol under certain conditions.[27]

3.1. ^{1}H NMR Spectra

Due to the ring current effect, NMR spectroscopy is a good method to study intramolecular interactions in porphyrins.[28] All these compounds have been characterized by ^{1}H NMR. For comparison, 4-chlorobutyl benzoate (compound **B1**) has been prepared. ^{1}H NMR spectra of **P1**, **B1** and **[ZnP1]** are shown in Fig. 1. The corresponding chemical shifts for ^{1}H NMR are listed in Table S1 in the supporting information. For **P1**, the signal at -2.67 ppm has been assigned to two inner NH protons, which is typical in free base porphyrin.[28] The signals of four protons at -0.58, -0.08, 0.33, 2.16 ppm are assigned to the butyl group. The corresponding resonances for the

compound **B1** are located at 4.35 (H2), 1.95 (H3 and H4) and 3.59 (H5) according to literature.[29] If we consider that the butyl group is located above the porphyrin plane in the crystal structure (*vide infra*), the porphyrin ring current effect will cause their resonances shift upfield. So these signals are assigned as shown in Figure 1. Their corresponding upfield shifts are 4.01, 2.51, 2.02 and 1.42 ppm comparing with compound **B1**. Such upfield shifts are similar to the case of 5-(8-ethoxycarbonyl-1-naphthyl) -10,15,20-triphenyl porphyrin (ENTPP).[6] For **[ZnP1]**, the resonances of butyl group have slight downfield shifts comparing with the compound **P1**. We notice there is one resonance at 1.20 ppm, which is caused by the residue H_2O in $CDCl_3$. It is generally at 1.50 ppm. The upfield shift for H_2O indicates the water molecule is coordinated to the zinc porphyrinate. As in our previous report on [Zn(ENTPP)(H_2O),[7] the crystal structure suggests H_2O is coordinated to zinc through the same side of the ester group. In our case, such coordination of H_2O could cause the butyl group away from the porphyrin plane, therefore lead to slightly downfield shifts of their ^{1}H NMR resonances.

3.2. *Molecular Structure*

One of the single crystals of **[ZnP1]** was measured by X-ray crystallography. Its structure was resolved in the space group $P2_1/c$. One asymmetric unit contains one complete porphyrin and one methylene chloride solvate. The structure of porphyrin is displayed in Fig. 2. It has one naphthyl and three phenyl groups on the *meso*-position. Zinc was inserted into the porphyrin core, and was coordinated by four pyrrole nitrogens. It is coplanar with four nitrogen (the

displacement out of four nitrogen plane is 0.03 Å), which is typical for four-coordinate species. The porphyrin core is quite planar with the maximum deviation of 24 atoms from the mean plane as 0.12 Ǻ (see Figure 3). Selected bond distances are listed in Table 2. The average Zn—N_p distance is 2.035(6) Ǻ, which is slightly shorter than that in five-coordinate zinc complexes.[7] Because of the constraint of naphthyl unit, the 8-position substituents, a chlorobutyl group, lies above the porphyrin plane (*vide supra*). The distances between C(2), C(3), C(4), C(5) and the porphyrin plane are 3.42, 3.56, 4.56 and 4.58 Ǻ, respectively.

4. Conclusion

In conclusion, the 4-chlorobutyl ester of CNTPP was synthesized. Its structure was confirmed by mass spectroscopy, ^{1}H NMR and X-ray crystallography. Such a product was formed by the acylative cleavage of tetrahydrofuran. Our study suggests the cleavage is promoted by Brønsted–Lowry acids. It provides a convenient method to prepare **P1**, a 4-chlorobutyl derivative of porphyrin with a four-carbon chain. Such a compound could also be used as a precursor for other derivatives of CNTPP.

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Supplementary material

Supplemental data is available at the publisher's website. Mass spectra and ^{1}H NMR are given in the supplementary material. CCDC 1007148 contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or by application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; deposit@ccdc.cam.ac.uk.

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Table 1. Crystallographic data for **[ZnP1]**.

Compound	[ZnP1]·CH_2Cl_2
Empirical formula	$C_{54}H_{39}Cl_3N_4O_2$
Formula weight	947.61
Temperature(K)	223(2) K
Wavelength(Å)	1.54178
Crystal system	Monoclinic
space group	$P2_1/c$
Unit cell dimensions	a =
	b =
	c =
	α = 90°
	β =
	γ = 90°
Volume ($Å^3$)	4496.87(15)
Z	4
ρ(g cm^{-3})	1.400
F(000)	1952
Crystal size(mm^3)	0.35 x 0.30 x
Theta range for data	3.65° to 70.00°
Limiting indices	-20<=h<=21
	-14<=k<=10
	-22<=l<=30
Reflections collected /	19172
Completeness to theta =	99.6 %
Data / restraints / parameters	8499 / 39/ 578
GOF	1.061
R_1,wR_2 [$I > 2\sigma(I)$]	R1 = 0.0546
	wR_2 = 0.1481
R_1,wR_2 (all data)	R_1 = 0.0663

	wR_2 = 0.1596
Largest diff. peak and	1.035 and

$R_1 = \sum(||F_0|-|F_c||)/\sum|F_0|$, $wR_2 = \sum w(|F_0|^2-|F_c|^2)^2/\sum w(|F_0|^2)^2]^{1/2}$

Table 2. Selected bond distances (Å) for **[ZnP1].**

Zn(1)–N(1)	2.031(2)	Zn(1)–N(2)	2.032(2)
Zn(1)–N(3)	2.044(2)	Zn(1)–N(4)	2.034(2)
N(1)–C(A1)	1.372(3)	N(1)–C(A2)	1.378(3)
N(2)–C(A3)	1.371(3)	N(2)–C(A4)	1.378(3)
N(3)–C(A5)	1.368(4)	N(3)–C(A6)	1.375(6)
N(4)–C(A7)	1.376(4)	N(4)–C(A8)	1.371(4)
C(1)–O(1)	1.202(4)	C(1)–O(2)	1.328(4)
C(2)–O(2)	1.460(4)	C(5)–Cl(1)	1.784(8)

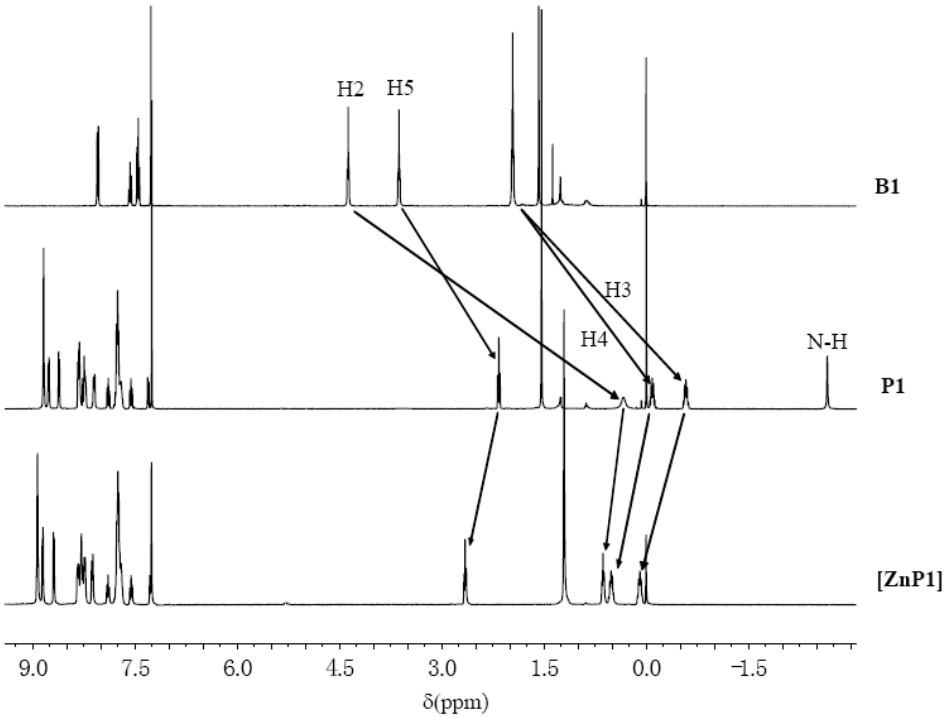


Figure 1. ^{1}H NMR spectra of **B1**, **P1** and **[ZnP1]** in $CDCl_3$.

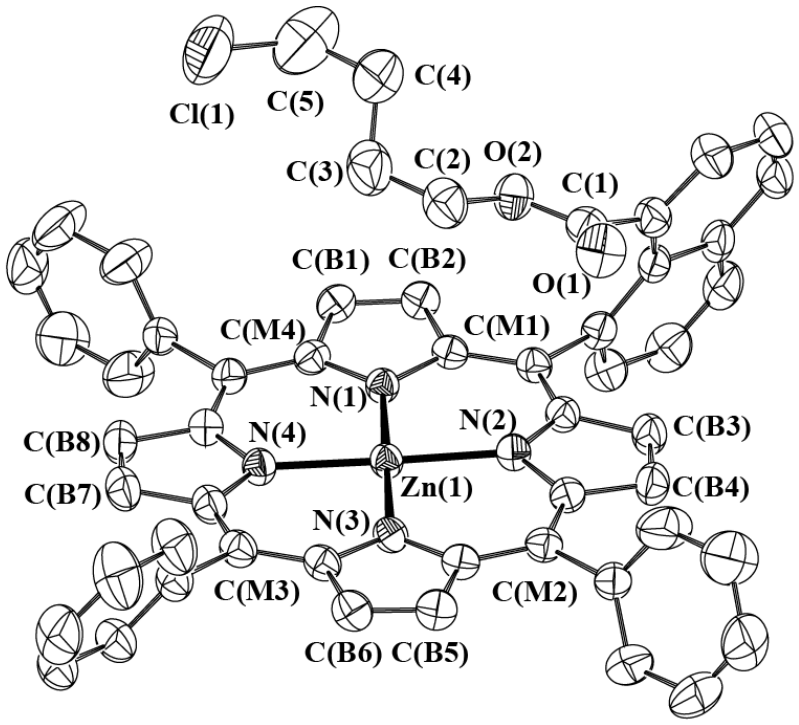


Figure 2. ORTEP diagram of **[ZnP1].** The hydrogen atoms of the porphyrin have been omitted for clarity. 50% probability ellipsoids are depicted.

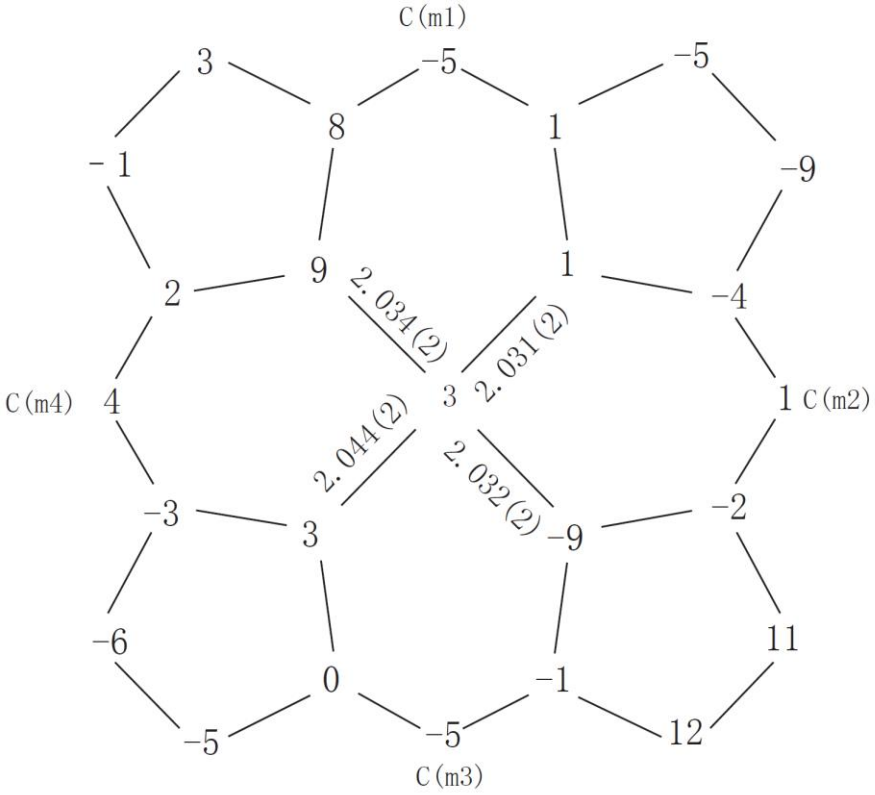
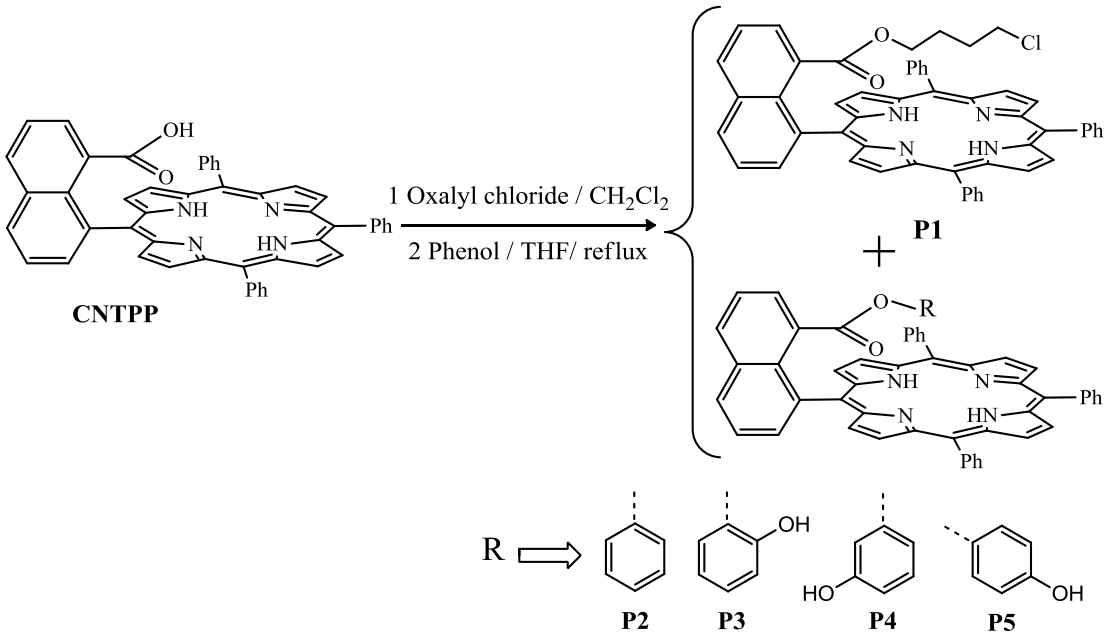
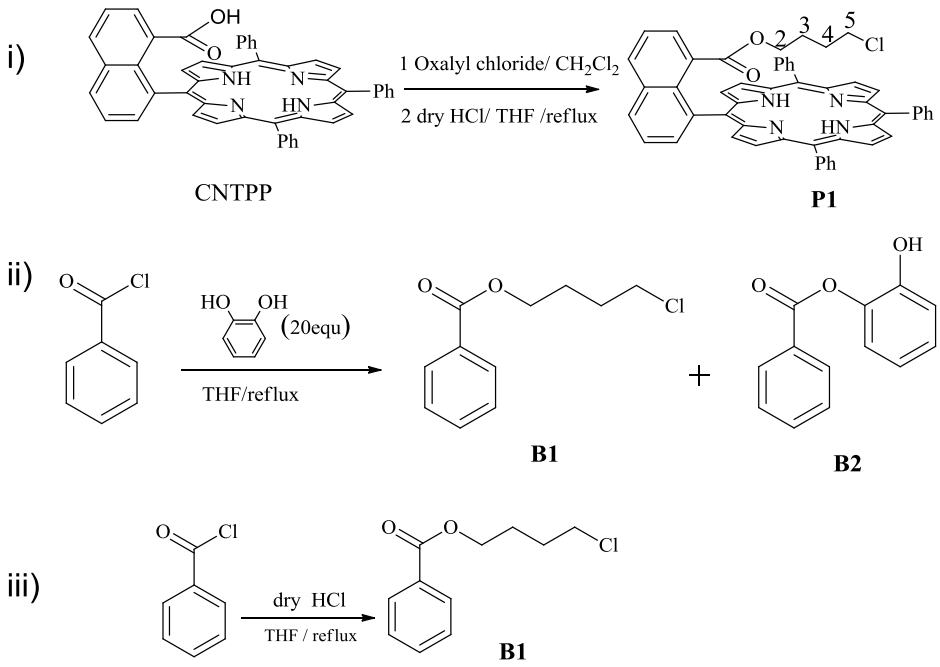


Figure 3. Formal diagrams of the porphyrinato cores for **[ZnP1].** Illustrated are the displacements of each atom from the mean plane of the 24 atom in units of 0.01 Å



Scheme 1. Synthetic route to the compound **P1** using phenols**.**



Scheme 2. i) Synthetic route to **P1** using dry HCl. ii) Synthetic route to **B1** by using catechol. iii) Synthetic route to **B1** by using dry HCl.