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Liquid state ^{15}N NMR studies of ^{15}N isotope labeled phthalocyanines

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Abstract: ^{15}N labeled soluble metallo- and metal-free phthalocyanines are described for the first time. The complexes were synthesized starting from phthalic anhydride derivatives using 98% ^{15}N enriched urea. The effects of the substitution pattern, aggregation, and coordinated metal on ^{15}N chemical shifts in liquid state NMR were studied.

Key words: Phthalocyanines, ^{15}N NMR, isotopic shifts, constitutional isomers

1. Introduction

Since their discovery at the beginning of the 20th century, phthalocyanines (Pcs) have been used as dyes and pigments.[1,2] Over the century since, they have found applications in a wide range of different fields such as photodynamic therapy, oxidation catalysts, and solar cells.[3–5]

The two NMR active nuclei of nitrogen, ^{15}N and ^{14}N, have isotopic abundances of 0.37% and 99.63%, respectively. The latter isotope with high natural abundance is more sensitive but it gives very broad lines due to its quadrupolar nature. An important disadvantage of ^{14}N signals is broadening up to kHz, which results in loss of resolution and useful information.[6] In this sense ^{15}N NMR lines are sharp but it suffers from insensitivity due to its low natural abundance. ^{15}N NMR is an especially important probe for biological research and the sensitivity problem has been overcome by labeling biological molecules with ^{15}N isotopes for NMR research.[7,8] ^{15}N NMR has also been a focus of interest in studies on coordination complexes with nitrogen donor ligands.[9] Due to their biological importance, ^{15}N labeled porphyrin derivatives, which can be considered analogues of Pcs coordinated to different metals, have been studied by ^{15}N NMR.[10]

In Pc chemistry, ^{15}N labeled unsubstituted copper(II) Pc is reported and the isotopic shifts of the IR and Raman bands are studied experimentally and theoretically.[11] Unsubstituted ^{15}N labeled metal-free Pc has been reported and the proton transfer mechanism has been investigated in solid state using high resolution ^{15}N and ^{13}C CPMAS NMR spectroscopy.[12] To the best of our knowledge, for the soluble Pcs liquid state ^{15}N NMR has not been reported to date.

In the present work, ^{15}N labeled tetra-tertbutyl zinc(II), nickel(II), and metal-free and bispyridine adduct of iron(II) Pcs as well as octa-substituted zinc(II) Pc carrying {4-(tert-butyl)phenoxy-} groups on peripheral positions were prepared. The synthesized complexes are 98% ^{15}N enriched and so their liquid state ^{15}N NMR measurements can be recorded and the results are discussed in terms of substitution pattern and coordinated metal ion.

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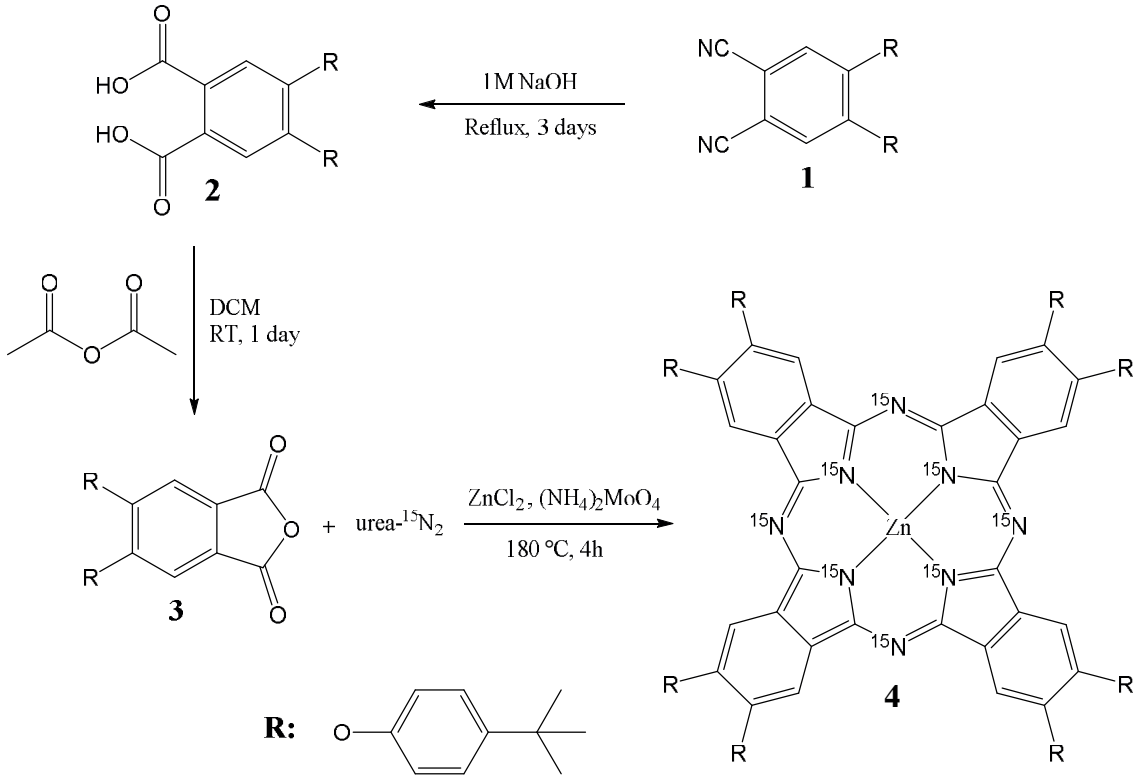
2. Results and discussion

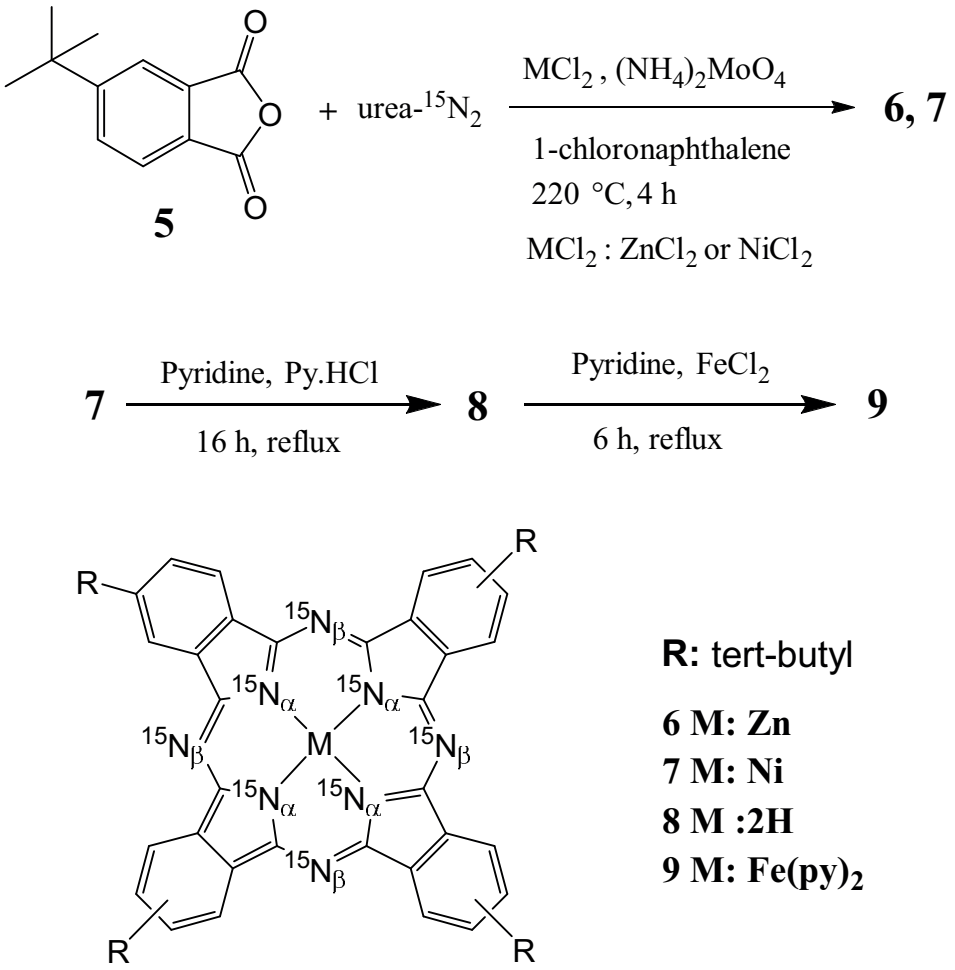
2.1. Synthesis and characterization

The synthetic path to octa-substituted Pc is shown in Scheme 1. First the dinitrile derivative **1** was hydrolyzed in basic conditions to obtain the phthalic acid derivative, which was further converted to anhydride derivative with acetic anhydride in dichloromethane. The synthesis of octa-substituted zinc(II) Pc was achieved by heating a mixture of 5,6-bis(4-(tert-butyl)phenoxy)phthalic anhydride, 98% ^{15}N enriched urea, anhydrous $ZnCl_2$, and a catalytic amount of ammonium molybdate (ca. 5%) without any solvent. Since the starting urea has 98% ^{15}N enriched the observed mass value for the product is $[M+8+H]^+$ with respect to the natural abundant derivative, i.e. the MALDI-TOF mass spectrum of complex **4** gave a single-charged ion peak m/z at 1770.232.



Scheme 1. Synthesis of **4**.

The synthesis of tetra-substituted Pcs is shown in Scheme 2. Tetra-tert-butyl substituted phthalocyanine derivatives have been studied intensively in the literature.[13] Most of the synthetic work was described starting from dinitril derivatives, but there are also some starting from anhydride derivative using urea as the nitrogen source.[14] In order to obtain the desired ^{15}N labeled molecules, we synthesized tetra-tert-butyl Zn(II) and Ni(II) phthalocyanines starting from 4-tert-butylphthalic anhydride using 98% ^{15}N enriched urea, which is commercially available. The synthesis of tetra-substituted Pcs **6** and **7** was achieved similarly to a reported procedure.[15] Metal-free Pc was obtained by demetalation of ^{15}N labeled zinc(II) Pc with hydrochloride salt of pyridine as reported earlier for nonlabeled Pc.[16] Iron(II) Pc was synthesized from metal-free Pc in pyridine and it was obtained as a bispyridine adduct.



Scheme 2. Synthesis of tetrasubstituted phthalocyanines (Py denotes pyridine, α and β nitrogen labels are shown used throughout this manuscript).

The MALDI-TOF spectra of synthesized complexes gave molecular ion peaks for **6**, **7**, and **8**, at m/z 808.415, 803.228, and 747.079, respectively. In the case of **9** the molecular ion peak was observed at 800.207 corresponding to iron(II) pc without pyridine adducts. In all of these phthalocyanines molecular ion peaks corresponding to $[M+8]^+$ of the natural abundant derivatives confirm the ^{15}N labeled products. In the FT-IR spectrum one easily identified difference for **8** from the natural abundant derivative was N–H stretching wave number, which was observed at 3283 cm^{-1} and which was shifted 8 cm^{-1} to lower wave number due to the ^{15}N isotopic effect.[16]

2.2. ^{15}N NMR studies of phthalocyanine compounds

Among the synthesized complexes in this work only **4** has a symmetrical substitution pattern and was obtained as a single isomer. On the other hand, Pcs containing one different substituent on each benzo unit are formed as a mixture of four constitutional isomers (Figure 1).[17–19]

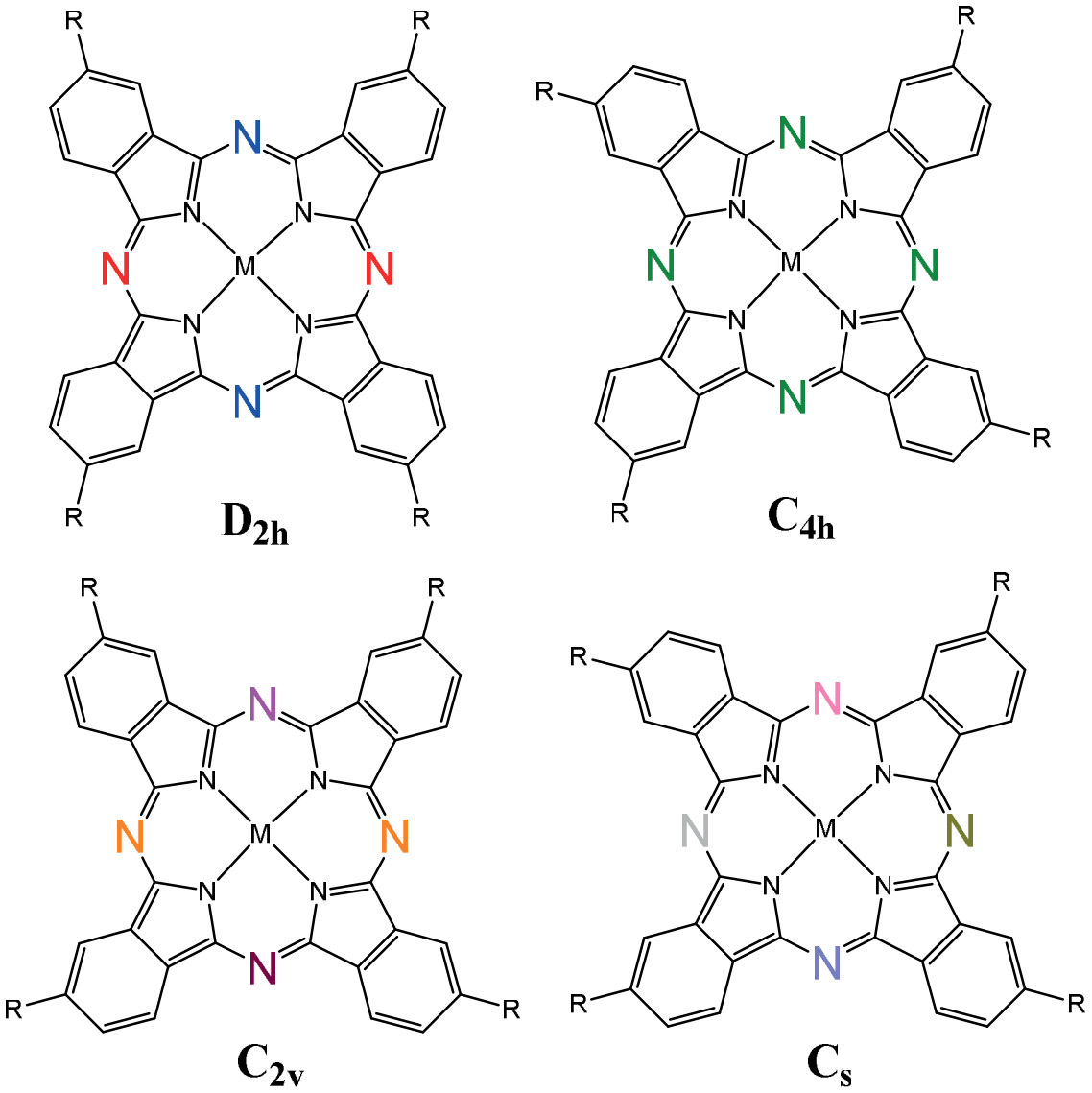


Figure 1. Constitutional isomers of tetrasubstituted phthalocyanines. (For each isomer symmetrically nonequivalent nitrogen atoms are shown in different colors for β-nitrogens).

^{15}N chemical shifts of octa-substituted **4** showed two sharp singlets for two types of nitrogen atoms on the Pc macrocycle and it was possible to identify unique ^{15}N chemical shifts. The comparison of the ^{15}N NMR of **4** and **6** noticeably shows the effect of symmetry and substitution on ^{15}N chemical shifts of the Pc core (Figure 2).

The isomer distribution of the product can vary as a consequence of the reaction conditions and the central metal as reported.[17] When all the isomers and their symmetries have been taken into account the statistical percentages of each isomer and the expected number of ^{15}N NMR signals for each α- and β-nitrogen of isomers and their relative intensities are summarized in Figure 3 inset. Therefore, one should expect 10 different chemical shifts for each α- and β-nitrogen unless they are not overlapped. Symmetrically nonequal β-nitrogen atoms for each isomer are highlighted in Figure 1.

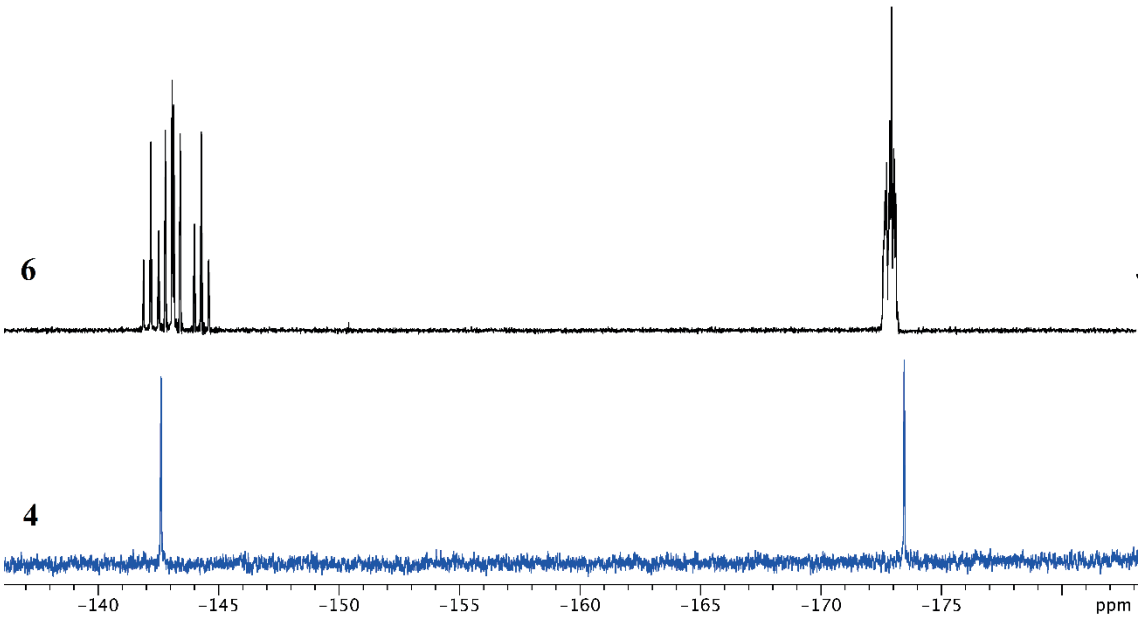
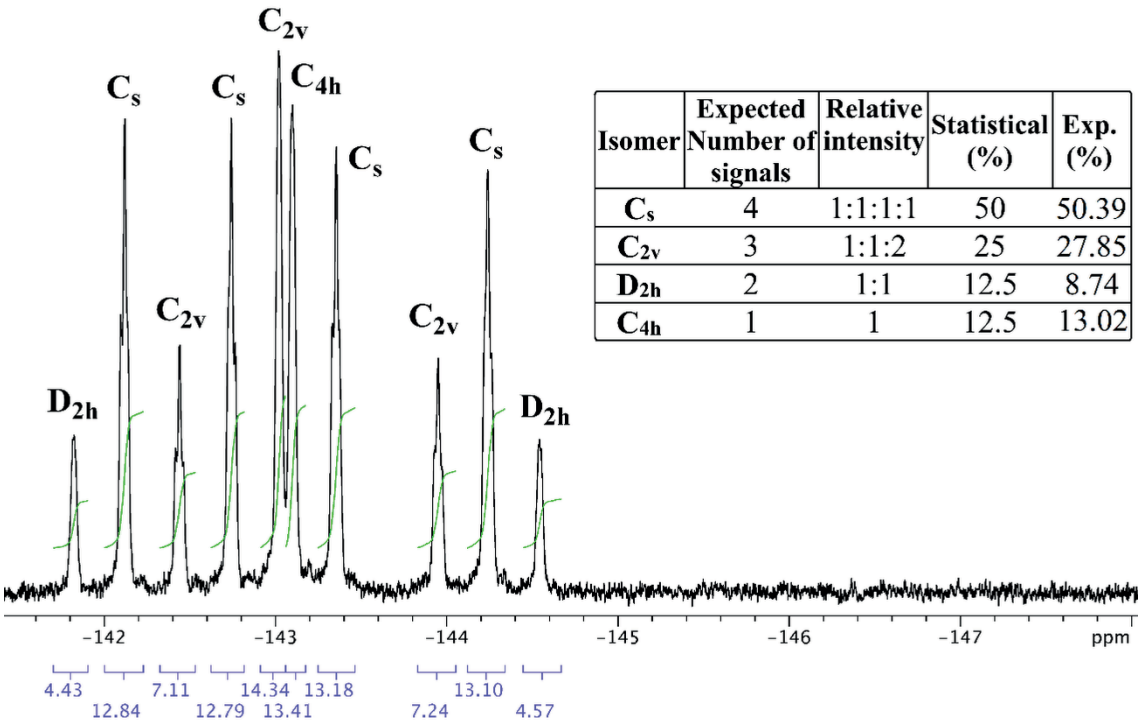


Figure 2. ^{15}N NMR of **4** and **6** ($CDCl_3$-pyridine-d_5).



Isomer	Expected Number of signals	Relative intensity	Statistical (%)	Exp. (%)
C_s	4	1:1:1:1	50	50.39
C_{2v}	3	1:1:2	25	27.85
D_{2h}	2	1:1	12.5	8.74
C_{4h}	1	1	12.5	13.02

Figure 3. α-Nitrogen ^{15}N NMR region of **6** (inset table shows expected number of signals in ^{15}N NMR and their relative intensities, statistically expected percentages of isomers and experimentally assigned percentages based on integration of the ^{15}N NMR spectra).

In ^{15}N NMR spectra of tetra-substituted complexes the best resolved spectra were observed for β-nitrogens of ZnPc (**6**) in $CDCl_3$ solution containing pyridine-d_5 and 10 different chemical shifts are observed

as expected (Figure 3). Based on the expectations, the assignment of each signal to isomers shows reasonable agreement with the observed ^{15}N NMR pattern. Although this can be considered somewhat ambiguous, from an NMR point of view it is interesting that slight differences in the chemical environment of the isomers can be clearly reflected in the large ^{15}N chemical shift range. The ^{15}N NMR chemical shift pattern resembles a fingerprint of the isomeric mixture. This result opens a new way to decide on the steric and electronic effect of various substituents on the symmetry of the Pc macrocycle with respect to differences in the ^{15}N chemical shifts. On the other hand, the signals are not resolved in the ^{15}N NMR region of α-nitrogens of **6** since they are observed as overlapped multiple signals; this implies that the substitution pattern is less effective on inner Pc nitrogens when compared with the outer Pc nitrogens in studied complexes.

^{15}N NMR spectra of the Pcs **6**, **7**, **8** and **9** are shown in Figure 4 and the observed chemical shifts are summarized in the Table. For the metal-free Pc (**8**) an α-nitrogen chemical shift was observed as a very broad signal due to N–H tautomerization.[12,20] A significant upfield shift is observed for α-nitrogens of NiPc (**7**) when compared to the other metallo- and metal-free Pc derivatives. This can be explained by the decrease in the contribution from the paramagnetic term in the shielding constant due to the strong Ni–N bond.[7] Similar upfield chemical shifts are also reported on α- and β-carbons of phthalocyanines to some extent in a decreasing fashion due to the distance from the metal center.[21] However, the chemical shift differences for the β-nitrogens that are three bonds away from the metal center are relatively minor for **6**, **7**, and **8**.

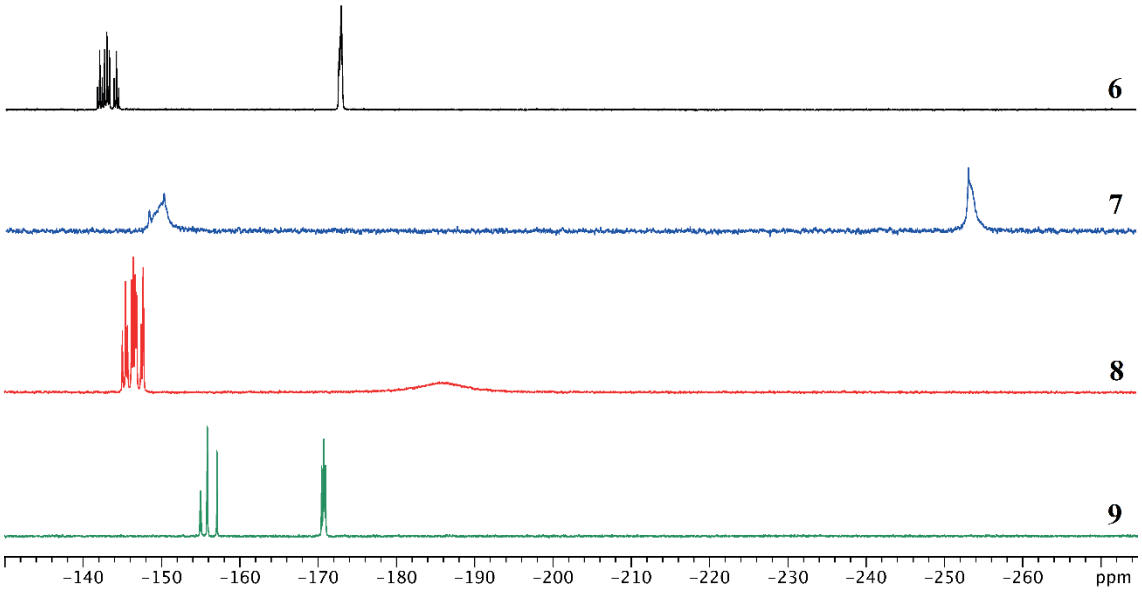


Figure 4. ^{15}N NMR of tetrasubstituted phthalocyanines in $CDCl_3$ (**6** contains one drop of pyridine-d_5 in $CDCl_3$).

Aggregation/disaggregation is a dynamic process in solution Pc chemistry.[22] In NMR spectroscopy when aggregation occurs it causes shorter nuclear relaxation times, and hence the NMR signals get broader.[23] The effect of aggregation on line broadening is clearly observed in ^{15}N NMR of **6** and **7** in $CDCl_3$. α- and β-nitrogens of the pc macrocycle are observed as broad signals and the slight differences in the chemical shifts are not resolved. A drop of deuterated pyridine was added to the **6** and **7** solutions in $CDCl_3$ to see the effect of axial coordination on aggregation of the Pcs; in the case of **6** aggregation is reduced due to the chemical

exchange of pyridine ligand, which interacts with the metal center from the axial position and the ^{15}N NMR signals are sharper and well resolved (Figure 5) but there was no such significant difference in the case of **7**.[24]

Table. Summary of observed ^{15}N chemical shifts of Pc complexes.

Complex	N_α (ppm)	N_β (ppm)
6 ($CDCl_3$)	–173.95	–144, –148 broad
6 ($CDCl_3$ + py-d_5)	–172.66, –173.232	–141.85, –142.15, –142.47, –142.77, –143.05, –143.13, –143.38, –143.98, –144.27, –144.57
7 ($CDCl_3$)	–253.098 broad	–147.89, –151.61
8 ($CDCl_3$)	–185.63 very broad	–145.03, –145.44, –145.68, –146.20, –146.44, –146.67, –146.84, –147.42, –147.69
9 ($CDCl_3$)	–170.51, –170.70, –170.76, –170.85, –171.00	–154.96, –155.02, –155.09, –155.88, –157.11
4 ($CDCl_3$ + py-d_5)	–173.48	–142.63

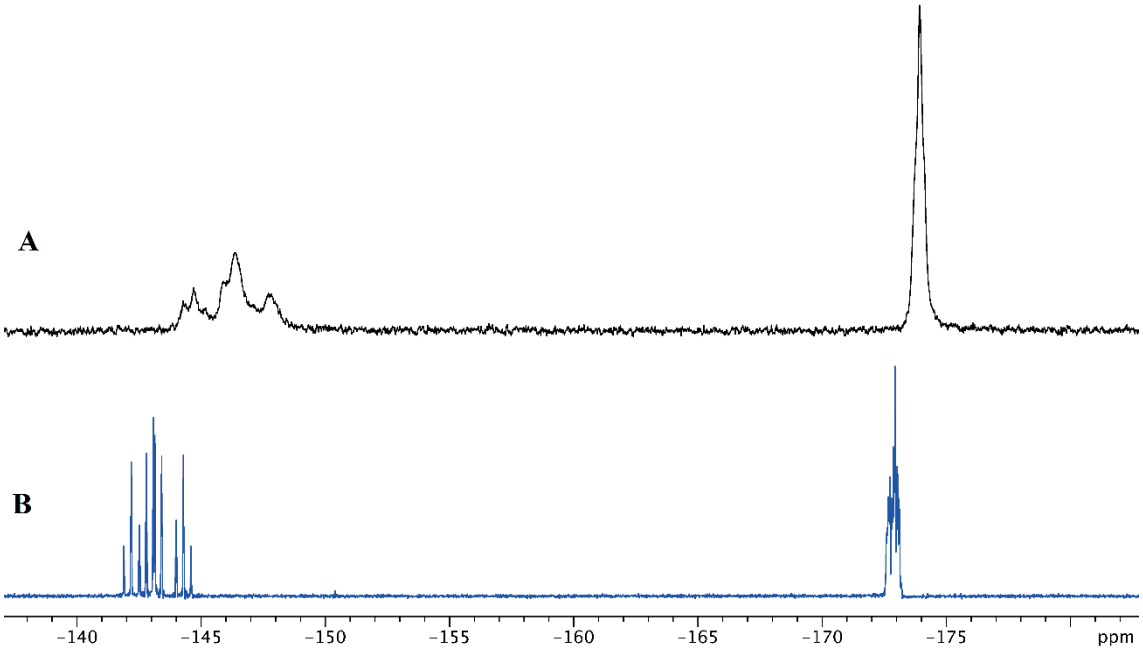


Figure 5. ^{15}N NMR spectra of **6** A) in $CDCl_3$ B) after addition of a drop of pyridine-d_5.

Iron(II) Pc (**9**) has two pyridine ligands coordinated to axial positions and it is structurally different from other metallo-phthalocyanine complexes. For this Pc complex aggregation is not expected due to axial coordination of pyridine. Line broadening of ^{15}N NMR signals is not observed for **9** in contrast to **6** and **7** in $CDCl_3$. α-Nitrogen of **9** was slightly shifted downfield with respect to **6** as reported in the case of similar porphyrin complexes.[25] β-Nitrogen of **9** shifted upfield with respect to **6**. The upfield shift on β-nitrogens of **9** with respect to **6**, **7**, and **8** is probably due to axial pyridine ligands. The X-ray diffraction studies of crystalline bispyridine iron(II) phthalocyanine shows ortho-hydrogens of the pyridine ligand in closer proximity to the meso-nitrogens of the pc macrocycle.[26] The ^{15}N chemical shift of coordinated pyridine nitrogen was indirectly determined from ^{1}H–^{15}N HMBC spectra. While the ^{15}N chemical shift of free pyridine in $CDCl_3$ is

given as –69 ppm, it has been shifted upwards to around –137 ppm in the case of bis(pyridine) adduct of iron (II) Pc (**9**).[27] This upfield shift is due to both coordination shift and ring current of the Pc macrocycle.

In conclusion, it has been accepted that the low natural abundance of ^{15}N restricts its use in routine NMR studies. However, in the present study it has been demonstrated that when it is enriched with ^{15}N alone, liquid state ^{15}N NMR could be a valuable tool giving rich information about the chemistry, structure, and solution behavior of phthalocyanine complexes.

3. Experimental

3.1. Materials and methods

IR spectra were recorded on a PerkinElmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. All NMR spectra were recorded on Agilent VNMRS 500 MHz at 25 °C and ^{1}H chemical shifts were referenced internally using the residual solvent resonances. ^{15}N chemical shifts were automatically measured with the standard VNMRJ software and they are given relative to nitromethane. Mass spectra were measured on a MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as the matrix. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. While 98% ^{15}N enriched urea was obtained from Sigma Aldrich, 4,5-bis(4-(tert-butyl)phenoxy)phthalonitrile (**1**) was synthesized according to the literature.[28]

3.2. Synthesis

3.2.1. Synthesis of 4,5-bis(4-(tert-butyl)phenoxy)phthalic acid (2)

4,5-Bis(4-(tert-butyl)phenoxy)phthalonitrile (**1**) (2 g, 4.7 mmol) was suspended in 250 mL of 1 M NaOH solution. The suspension was refluxed for 3 days. After the solution was cooled to room temperature, pH of the mixture was adjusted to 5 by adding 1 M HCl. The white precipitate was filtered and washed with water and then dried under reduced pressure. The product was obtained as a white solid.

Yield: 1.95 g, 90%. FTIR (ν, cm^{-1}): 3070, 2964, 2904, 2869, 1696, 1643, 1591, 1568, 1505, 1389, 1276, 1211, 1067, 829. ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.47 (4H, d, J = 8.77 Hz) 7.14 (2H, s) 7.04 (4H, d, J = 8.77 Hz), 1.37 (18H, s). ^{13}C NMR (126 MHz, $CDCl_3$)δ 152.2, 151.5, 149.1, 127.4, 121.3, 119.6, 115.2, 109.8, 34.6, 31.4.

3.2.2. 5,6-Bis(4-(tert-butyl)phenoxy)phthalic anhydride (3)

To a solution of 4,5-bis(4-(tert-butyl)phenoxy)phthalic acid (**2**) (1 g, 4.32 mmol) in 20 mL of dichloromethane, 2 mL of acetic anhydride (21.6 mmol) was added and then stirred at room temperature for 1 day. The solvent was evaporated under reduced pressure. The product was obtained as a white solid.

Yield: 0.93 g, 97%. FTIR (ν, cm^{-1}): 3047, 2963, 2906, 2870, 1843, 1772, 1584, 1490, 1442, 1360, 1268, 1236, 1099, 1073. ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.48 (4H, m), 7.34 (2H, s), 7.07 (4H, m), 1.38 (18H, s). ^{13}C NMR (126 MHz, $CDCl_3$)δ 162.5, 155.5, 151.9, 149.0, 127.4, 125.5, 119.8, 112.7, 34.6, 31.4.

3.2.3. 2,3,9,10,16,17,23,24-Octakis[(4-tert-butyl)phenoxy]phthalocyaninatozinc(II)-$^{15}N_8$ (4)

5,6-Bis(4-(tert-butyl)phenoxy)phthalic anhydride (**3**) (0.113 g 0.25 mmol), $^{15}N_2$-urea (0.125 g 2 mmol), zinc chloride (0.013 g, 0.1 mmol), and 5% of the stoichiometric amount of ammonium molybdate were mixed. The

mixture was heated slowly to 180 °C over 2 h and kept at this temperature for a further 2 h. After the reaction mixture was cooled to room temperature 50 mL of petroleum ether was added and the mixture was filtered. The filtrate was discarded and the brownish-green solution was dried under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane 1/4). The zinc phthalocyanine was obtained as a blue-green solid.

Yield ~1 mg, ~1%. ^{1}H NMR (500 MHz, $CDCl_3$)δ 8.99 (8H, s), 7.37 (16H, m), 7.13 (16H, m), 1.33 (72H, s). Maldi-Tof MS m/z: 1770.232 $[M+H]^+$.

3.2.4. General procedure for the preparation of ^{15}N enriched tetra-tert-butyl Zn(II) and Ni(II) phthalocyanines

4-tert-Butylphthalic anhydride (**5**) (1 eq), urea-$^{15}N_2$ (4 eq), metal salt (0.3 eq) ($ZnCl_2$ or $NiCl_2$), and 5% of the stoichiometric amount of ammonium molybdate were suspended in 1-chloronaphthalene and the temperature was slowly raised to 220 °C over 2 h. The reaction mixture was stirred for 2 h at this temperature. After the reaction mixture was cooled to room temperature, it was diluted with petroleum ether and filtered. The filtrate was dried under vacuum. The products were purified with column chromatography using silica gel and an ethyl acetate/hexane (1/3) mixture and obtained as a mixture of four constitutional isomers. Both products were obtained as blue solids.

3.2.4.1. 2,9(10),16(17),23(24)-Tetra(tert-butyl)phthalocyaninatozinc(II)-$^{15}N_8$ (6)

Yield: 27%. FTIR (ν, cm^{-1}): 3071, 2956, 2904, 2867, 1616, 1487, 1324, 1255, 1082, 912, 828, 739. ^{1}H NMR (500 MHz, $CDCl_3$-Pyridine-d_5): δ, ppm 9.52 (4H, b, Pc-H), 9.40 (4H, m, Pc-H), 8.24 (4H, m, Pc-H), 1.77 (36H, m, C-$(CH_3)_3$), MS: m/z 808.415 M^+.

3.2.4.2. 2,9(10),16(17),23(24)-Tetra(tert-butyl)phthalocyaninatonickel(II)-$^{15}N_8$ (7)

Yield 21%, FTIR (ν, cm^{-1}): 3071, 2955, 2920, 2865, 1617, 1528, 1486, 1327, 1258, 1084, 825, 744. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 8.73–7.77 (12H, b, Pc-H), 1.91–1.80 (36H, m, C-$(CH_3)_3$). MS: m/z 803.828 $[M+H]^+$.

3.2.5. 2,9(10),16(17),23(24)-Tetra(tert-butyl)phthalocyanine-$^{15}N_8$ (8)

Zinc phthalocyanine (**6**) (40 mg, 0.05 mmol) and pyridine.HCl (1 g, 8.7 mmol) were dissolved in 5 mL of pyridine and the mixture was refluxed under N_2 for 16 h. After the reaction mixture was cooled to room temperature, 10 mL of water was added and the product was precipitated. The precipitate was washed first with water and then with methanol. After drying in vacuo the product was purified by column chromatography on silica gel by using ethyl acetate/hexane (1/3) eluent. The product was obtained as a dark blue solid.

Yield 74%, FTIR (ν, cm^{-1}): 3283, 3071, 2956, 2907, 2866, 1617, 1485, 1258, 1089, 1000, 827, 741. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 9.14–8.62 (8H, m, Pc-H), 8.17–8.04 (4H, m, Pc-H), 1.94–1.89 (36H, m, C-$(CH_3)_3$), –2.67– –3.46 (2H, m, N-H), MS: m/z 747.079 $[M+H]^+$.

3.2.6. Bispyridine-2,9(10),16(17),23(24)-tetra(tert-butyl)phthalocyaninatoiron(II)-$^{15}N_8$, (9)

A mixture of ^{15}N labeled tetra-tertbutyl-phthalocyanine (**8**) (20 mg, 0.027 mmol) and anhydrous $FeCl_2$ (10 mg 0.08 mmol) was refluxed in distilled and dry pyridine for 6 h under nitrogen. After the reaction mixture was cooled to room temperature, it was poured into water and then the precipitate was filtered and dried under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane, 1/3). The product was obtained as a blue solid.

Yield: MS: 19 mg, 74%, ^{1}H NMR (500 MHz, $CDCl_3$) 9.36 (4H, m, Pc-H), 9.24 (4H, m, Pc-H), 8.04 (4H, m, Pc-H), 5.83 (2H, t, py-γ-H, J = 7.49), δ 4.59 (4H, t, Py-β-H, J = 7.1), 2.15 (4H, d, Py-α-H, J = 5.5), 1.77 (36H, m, C-$(CH_3)_3$). m/z 800.207 $[M\text{-}2Py]^+$, 817.258 $[M\text{-}2Py\text{+}OH]^+$.

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