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Coordination Polymers Based on Aluminum(III) Porphyrins

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Aluminum(III) porphyrin carboxylate complexes have shown an affinity for a sixth nitrogenous ligand. The use of isonicotinic or nicotinic acid, which offers both a carboxylate and a nitrogen donor in the same molecule, resulted in the formation of one-dimensional (1-D) coordination polymers. The complexes and their linear oligomers have been characterized by ^{1}H NMR spectroscopy and nanoelectrospray ionization spectrometry. X-ray analyses confirmed the formation of the 1-D polymers in the solid state.

Introduction

The use of axial coordination to metalloporphyrins has long been an attractive approach for the generation of multiporphyrin arrays because the knowledge of a metalloporphyrin's preferred coordination number, geometry, and ligand preference allows one to rationally construct arrays with well-defined geometries.[1] One-dimensional (1-D) "shish kebab" coordination polymers containing metalloporphyrins and bridging ligands have shown promise as conductive polymers.[2] To date, much of the attention of these 1-D coordination polymers has been paid to metalloporphyrins containing iron(II)/iron(III), ruthenium(II), osmium(II), and cobalt(II) metal centers.[3] Symmetrical bridging ligands such as 4,4′-bypyridine or 1,4-diazabicyclo[2.2.2]octane have often been used,[4] but reports using unsymmetrical bridging ligands are less common.[5] Recently, we described the use of aluminum(III) benzoate complexes as supramolecular blocks that showed a preference for binding nitrogenous ligands in the vacant axial site.[6] We reasoned that the simple marriage of the carboxylate unit and a nitrogen donor, through the use of isonicotinic or nicotinic acid, would result in polymeric precursors capable of forming 1-D coordination polymers (Scheme 1). Herein we report the synthesis and characterization of aluminum(III) porphyrin building blocks **1-*Isonic*** and **1-*Nic*** as well as solution and solid-state evidence for the corresponding 1-D coordination polymers.

Results and Discussion

The synthesis of **1-*Isonic*** and **1-*Nic*** proceeds smoothly upon the addition of excess isonicotinic or nicotinic acid to

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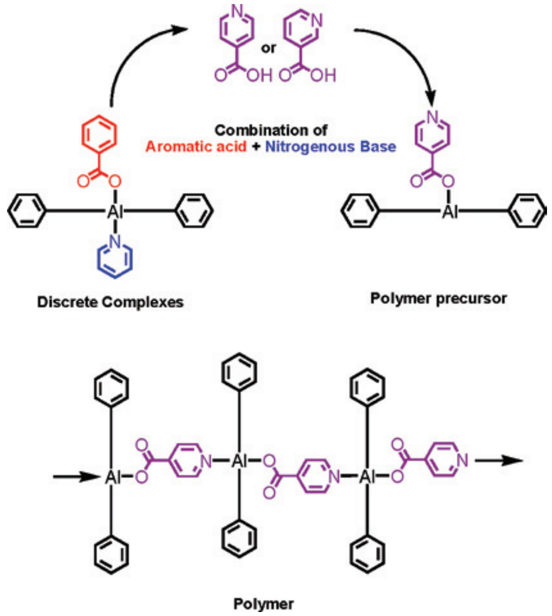
Scheme 1. Construction of "Shish Kebab" Coordination Polymers Using Aluminum(III) Porphyrins



a chloroform solution of **1-*OH*** (Figure 1). Because of the low solubility of the acids in chloroform, the desired complexes could be easily isolated in quantitative yield following filtration, to remove the excess acid, and evaporation. The ^{1}H NMR spectrum confirmed the coordination of the axially bound isonicotinate or nicotinate by the upfield shift of the proton resonances due to the shielding effect of the porphyrin. In both cases, the signals associated with the aromatic acid are broad at room temperature (Figure 2, top and middle). This is due to the coordination, which is fast on the chemical shift time scale, of the pyridine nitrogen of one complex to the vacant axial site on the aluminum(III) center of another complex, consistent with the formation of small linear oligomers in solution. Further evidence of linear oligomer formation in solution was seen by varying the concentration. Figure 2 (middle and bottom) shows the ^{1}H NMR spectra of **1-*Isonic*** at 5 and 15 mM. It can be seen that all of the proton resonances are shifted upfield as the concentration is increased. As expected, the proton labeled α_{pyr} has a larger $\Delta\delta$ response at 0.7 ppm, as compared to a $\Delta\delta$ of 0.26 ppm for β_{pyr}. This is due to the greater shielding effects experienced by α_{pyr} as a result of the distance to the other aluminum(III) porphyrin complex. A similar but smaller response to an increase in the concentration was also seen for **1-*Nic*** (see the Supporting Information).

Variable-temperature ^{1}H NMR spectroscopy was also employed to confirm the formation of linear oligomers in solution. Figure 3 shows the ^{1}H NMR spectra of **1-*Isonic*** at 223, 293, and 323 K at 15 mM. At 323 K, the resonances for α_{pyr} and β_{pyr} become sharp, consistent with the presence

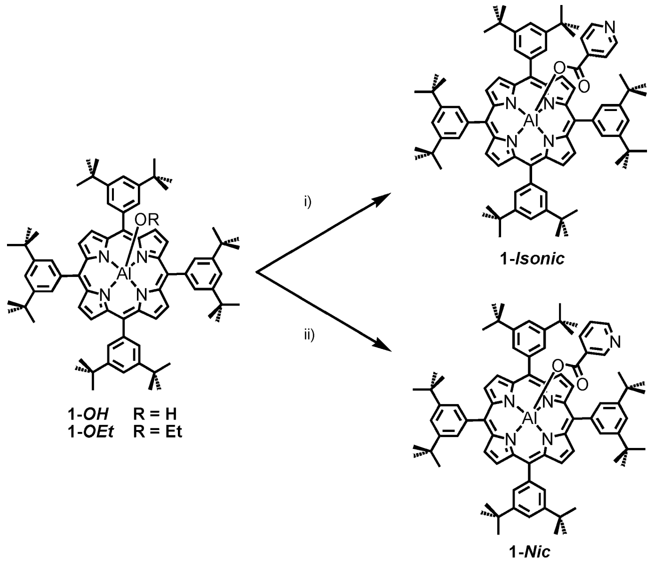


Figure 1. Synthesis of aluminum(III) porphyrins: **1-*Isonic***, (i) CHCl$_3$/isonicotinic acid, 12 h, room temperature; **1-*Nic***, (ii) CHCl$_3$/nicotinic acid, 12 h, room temperature.

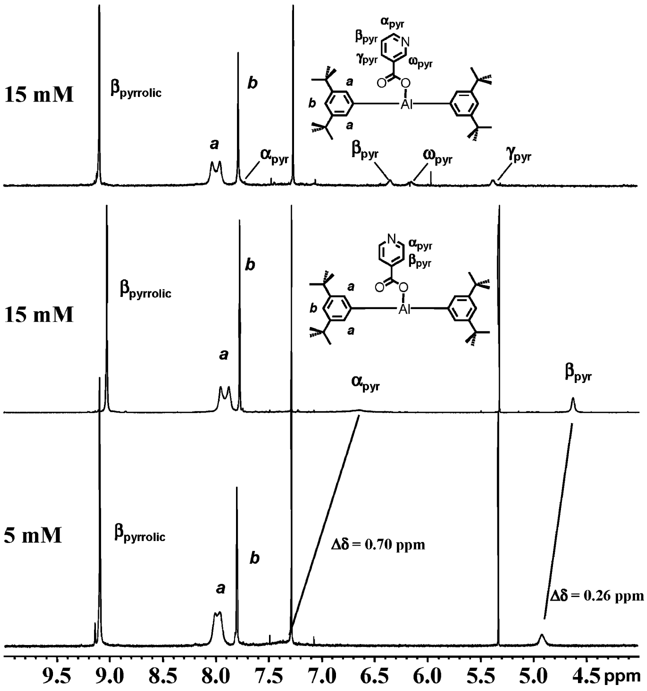


Figure 2. ^{1}H NMR spectra of **1-*Nic*** (top) and **1-*Isonic*** (middle) at a concentration of 15 mM and ^{1}H NMR spectrum of **1-*Isonic*** at a concentration of 5 mM (bottom). Spectra were recorded in CDCl$_3$ at 500 MHz (300 K). The peak at ~5.3 ppm is due to CH$_2$Cl$_2$.

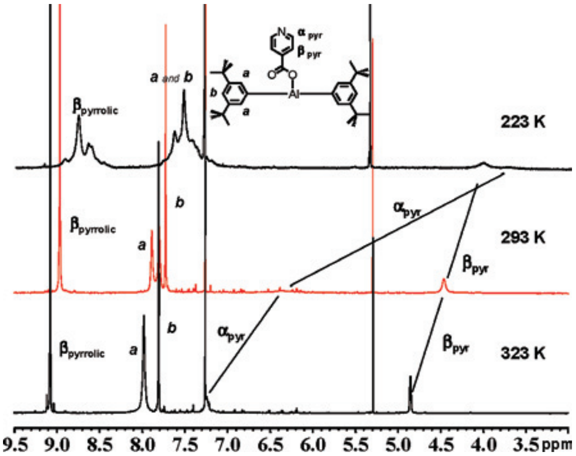


Figure 3. Variable-temperature ^{1}H NMR spectra of **1-*Isonic*** at 223 K (top), 293 K (middle), and 323 K (bottom). Spectra were recorded in CDCl$_3$ at 500 MHz (15 mM). The peak at ~5.3 ppm is due to CH$_2$Cl$_2$.

of mostly monomer in solution. As the temperature is lowered, all of the resonances shift upfield. At 223 K, many of the resonances are split, indicating an inequivalence likely due to a restriction of spinning about the vertical axis of individual porphyrin units within the higher order linear oligomers. This is due to the interdigitation of *tert*-butyl groups of adjacent porphyrins, generating a gearing effect and hindering rotation. At this temperature, the signal of α_{pyr} has moved upfield to that of β_{pyr}. It is expected that the chemical shift of the α_{pyr} resonance will be further upfield as compared to the β_{pyr} resonance because of its close proximity to the plane of the porphyrin, upon coordination to another monomer. Again, a similar but smaller dependence on the temperature was seen for **1-*Nic***. We believe that this is related to the conformation required for coordination. The nicotinate ligand must "bend back" to expose the nitrogen for coordination to another aluminum center. This additional requirement results in a shorter distance between porphyrin planes and an enhanced "steric" effect, which makes oligomer formation less sensitive to the temperature and concentration. We believe that only linear oligomers are possible because of the bulk of the 3,5-di-*tert*-butylphenyl group in the meso positions, preventing the formation of cyclic coordination polymers.

UV/vis spectroscopy for both **1-*Isonic*** and **1-*Nic*** showed the expected Soret band at 418 nm and one significant Q band at 548 nm. Not surprisingly, a low concentration of 2×10^{-6} M was required for the analysis, and no linear oligomers were detected in the UV/vis spectrum, as judged by the absence of a red-shifted Soret band due to pyridine coordination or shifting of the Soret band as a result of exciton coupling.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) also confirmed the expected structures of **1-*Isonic*** and **1-*Nic*** with masses of *m*/*z* 1209.54 and 1209.51, respectively, in good agreement with the expected value of *m*/*z* 1209.73 for both. No additional peaks for dimers or higher oligomers were detected. However, using a nanoelectrospray ionization (nano-ESI)[7] mass spectrometer, modified for high mass measurements, it was possible to observe higher oligomers for both the **1-*Isonic*** and **1-*Nic*** porphyrin complexes. The highest oligomer observed for **1-*Isonic*** was an octamer with peaks detected at *m*/*z* 9689 and 9567 corresponding to the octamer with and without the terminal isonicotinic ligand (Figure 4). The largest oligomeric state for **1-*Nic*** clearly observed was a hexamer. In order to verify that the complexes formed from **1-*Isonic*** and **1-*Nic*** were specific rather than as a result of the droplet evaporation and fission in the electrospray process, a control porphyrin **1-*OEt*** with limited oligomerizing ability was infused into the mass spectrometer at the same concentration from the same electrospray capillary as that of **1-*Isonic*** or **1-*Nic***. MS spectra of **1-*Isonic*** or **1-*Nic*** sprayed simultaneously and under conditions identical with those of the control porphyrin illustrated the greater sample oligomerization of **1-*Isonic*** and **1-*Nic*** compared to the control. Figure 5 illustrates the greater oligomerization of **1-*Isonic*** compared to that of **1-*OEt***, with oligomers of **1-*Isonic*** dominating this spectrum except in the case of the monomeric species, for which the most intense peak (*m*/*z*1106) corresponds to the mass of **1-*Isonic*** or **1-*OEt*** without the isonicotinic ligand but with a water molecule in this now free coordination site. Additionally, the relatively significant peak at *m*/*z* 2222 corresponds to the mass of two **1-*OEt*** porphyrins without the terminal ligand; this peak is likely the result of a nonspecific association resulting from the concentration of the sample combined with the electrospray process;[8] no further oligomerization of the **1-*OEt*** species is observed above the dimer, highlighting the specificity of the oligomerization of **1-*Isonic***. Identical control experiments for **1-*Nic*** and **1-*OEt*** were also performed, giving similar findings (data not shown). Furthermore, simulated peak intensities for the control experiments if oligomerization of **1-*OEt*** and **1-*Isonic*** or **1-*Nic*** were equally likely are compared to the actual peak intensities and demonstrate that **1-*Isonic*** and **1-*Nic*** do exhibit selectivity in oligomerization (see the Supporting Information).

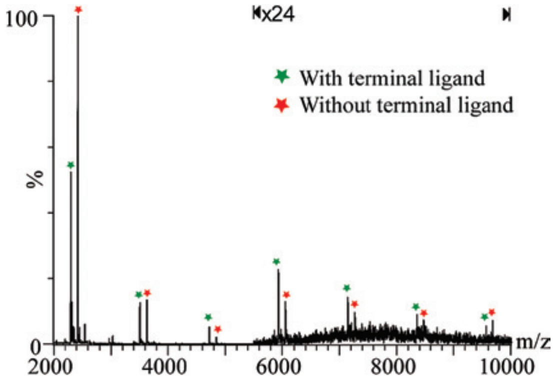


Figure 4. Nano-ESI MS spectrum of **1-*Isonic*** oligomers in toluene.

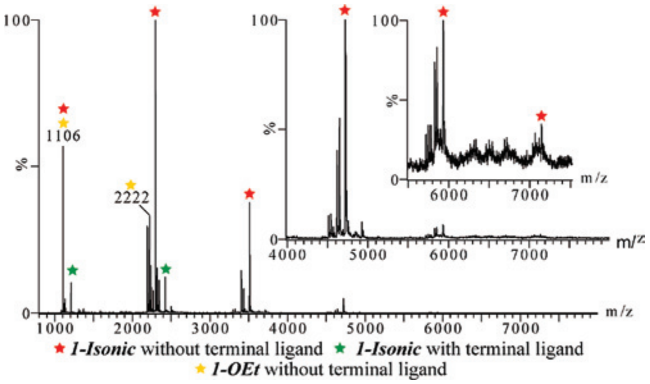


Figure 5. Nano-ESI MS spectrum of **1-*Isonic*** and **1-*OEt*** infused simultaneously at the same concentration (2 mM) under identical MS conditions. No peaks were observed for **1-*OEt*** with the terminal isonicotinic ligand.

Single-crystal X-ray analysis was performed on small, weakly diffracting crystals of both complexes using synchrotron radiation. Crystals of **1-*Isonic*** and **1-*Nic*** suitable for analysis were grown from slow diffusion of hexane into a solution of chloroform/dichloromethane. Both crystallize

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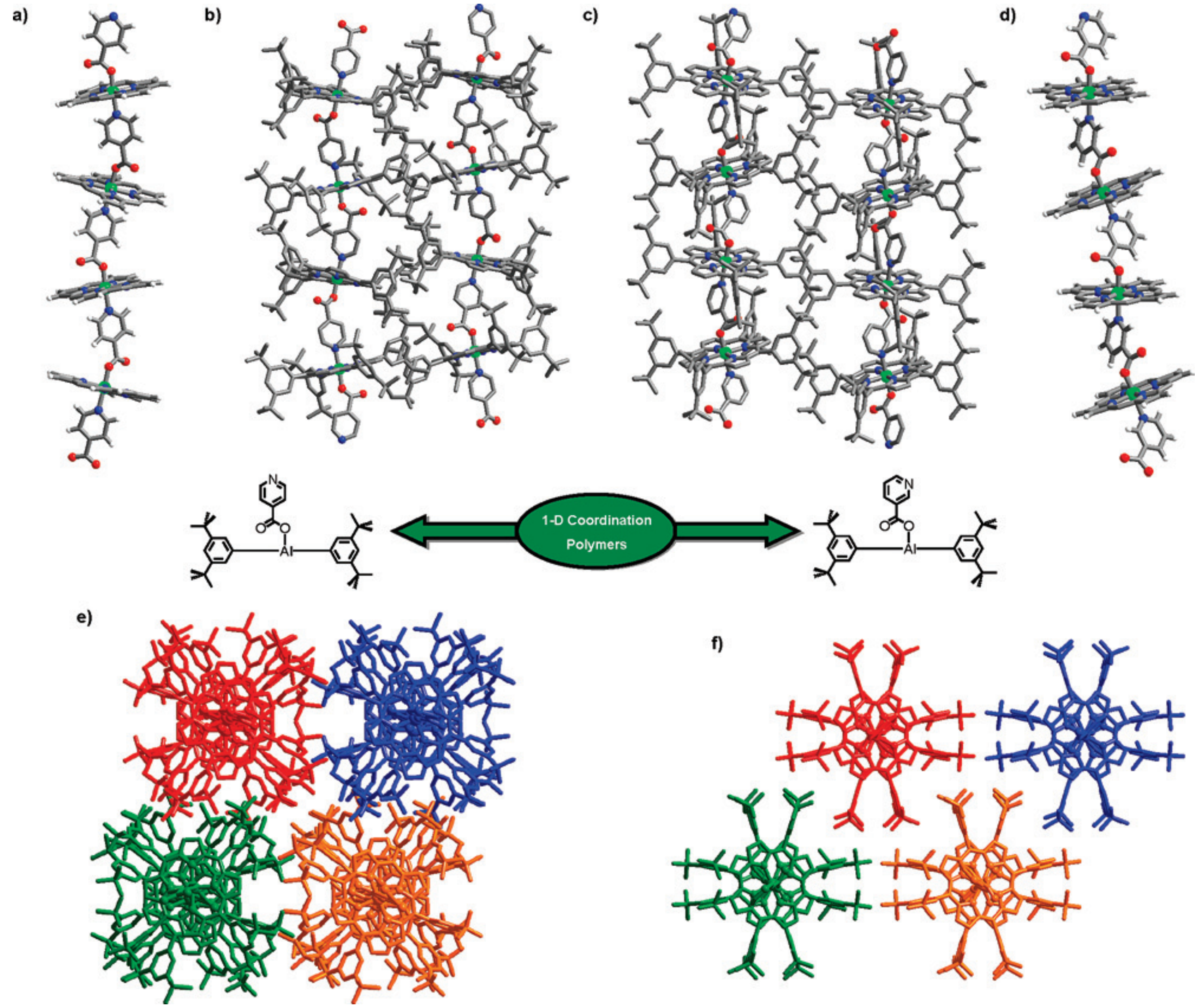

Figure 6. (a) Structure of a single strand of **1-*Isonic*** (meso subsituents and hydrogens removed for clarity). (b) Two adjacent strands of **1-*Isonic*** emphasizing the antiparallel alignment. (c) Two adjacent strands of **1-*Nic*** emphasizing the antiparallel alignment. (d) Structure of a single strand of **1-*Nic*** (meso subsituents and hydrogens removed for clarity). (e) Interstrand packing as viewed along the *c* axis for **1-*Isonic***. (f) Interstrand packing as viewed along the *c* axis for **1-*Nic***.

in space group $P2_1/c$, with disordered molecules of chloroform and dichloromethane (**1-*Isonic***) and chloroform, hexane, and water (**1-*Nic***) in the crystal lattices. In the crystal, the asymmetric unit of **1-*Isonic*** contains two aluminum porphyrin units linked by an isonicotinic acid group, which, under crystal symmetry, generates the expected 1-D coordination polymer, as shown in Figure 6a. Each aluminum is bound to the four porphyrin nitrogen atoms, a carboxylate oxygen, and the nitrogen of the coordinated isonicotinic building block, to generate a *pseudo*octahedral arrangement at the aluminum center. The polymeric strands are oriented along the *c* axis (Figure 6e). As expected, within each polymeric strand, the isonicotinates are aligned in one direction. However, because of space group symmetry, in the adjacent strand the isonicotinates are aligned in the opposite direction, leading to an overall antiparallel alignment (Figure 6b).

The crystal structure of **1-*Nic*** revealed the expected 1-D coordination polymer, as shown in Figure 6d, with the asymmetric unit containing one octahedrally coordinated aluminum center. The aluminum is bound to the four nitrogens of the porphyrin, the nicotinate oxygen, and the nitrogen of the coordinated nicotinic building block. The polymeric strands are oriented along the *c* axis with an AB style repeat unit (Figure 6f). As expected, within each polymeric strand, the nicotinates are aligned in one direction yet, as with **1-*Isonic***, because of the space group symmetry, adjacent strands run in the opposite direction, leading to an overall antiparallel alignment (Figure 6c).

A comparison of **1-*Nic*** and **1-*Isonic*** shows aluminum−aluminum distances of 8.363(1) and 8.830(3) Å, respectively. The shorter aluminum−aluminum distance for **1-*Nic*** is expected because the nicotinate must bend back to coordinate the aluminum center. Neighboring porphyrins within a strand do not lie parallel in relation to each other but instead adopt a nonparallel arrangement, resulting in planar angles of 18.3° for **1-*Nic*** and 24.5° for **1-*Isonic*** (Figure 7a,b). This results in a zigzaging of the porphyrin planes within each strand and also an alternating interdigitation of the *tert*-butyl groups, on the meso substituents. The interdigitation of the *tert*-butyl

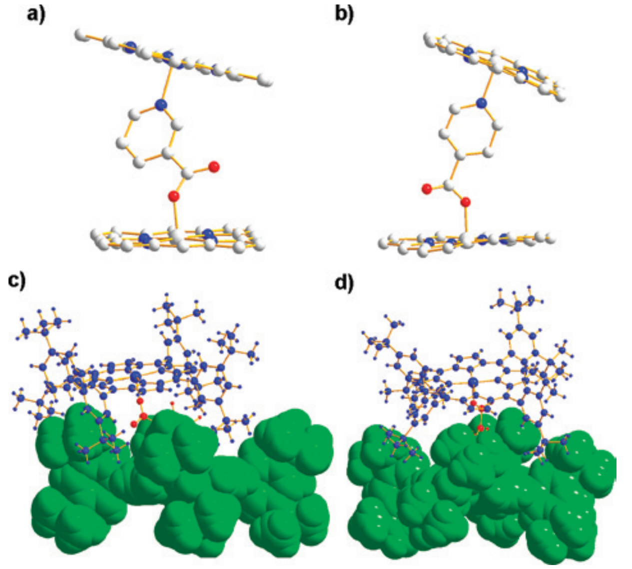

Figure 7. (a and b) Ball-and-stick representations of **1-*Nic*** and **1-*Isonic*** showing the bridging ligand sandwiched between two porphyrins within the polymer strand. Combination of a ball-and-stick and space-filling representation showing the interpenetration of the *tert*-butyl groups within the polymer, for **1-*Nic*** (c) and **1-*Isonic*** (d).

groups, as shown in Figure 7c,d for **1-*Nic*** and **1-*Isonic***, is the result of a favorable van der Waals interaction.

The results presented here indicate that the use of ligands exhibiting other spatial relationships between oxygen and nitrogen donors should lead to the generation of a range of new geometries for the porphyrin coordination polymers.

Experimental Section

Compound **1-*OEt*** was prepared similarly to that of **1-*OH***, but the reaction was quenched with ethanol.[6] ^{1}H NMR spectra were obtained on a Bruker Avance 500 instrument operating at 500.1 MHz (using the deuterated solvent as the lock and the residual solvent or tetramethylsilane as the internal reference). The ^{1}H NMR spectra were recorded at 15 mM unless otherwise stated. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. MALDI-TOF MS spectra were recorded on a 4700 Proteomics analyzer (Applied Biosystems) with TOF/TOF optics. The spectra were acquired in reflector mode, and 1000 laser shots were averaged together. UV/vis spectra were obtained on a Hewlett-Packard 8452A diode-array spectrometer using a 1-cm-path-length quartz cell versus a pure-solvent reference. The absorption spectra were recorded in dichloromethane at concentrations of 2.0×10^{-6} M.

Nano-ESI MS spectra were acquired on a modified[9] TOF LCT instrument (Micromass, Manchester, U.K.) under conditions optimized for the transmission of noncovalent complexes. Gold-coated nano-ESI capillaries were prepared in-house using a micropipette puller (Flaming/Brown P-97, Sutter Instruments, Novato, CA) and borosilicate glass tubes (Harvard Apparatus, Holliston, MA) as described previously.[10] The pulled ends of the capillaries were clipped under a stereomicroscope, resulting in an inner tip diameter of between 2 and 5 μM. Capillary needles were loaded, using GEloader tips (Eppendorf), with typically 2 μL of the porphyrin solution in toluene (Romil, Cambridge, U.K.), concentration 2 mM, which was sprayed from these capillaries with a nitrogen backing pressure to aid stable flow. **1-*Isonic*** and **1-*Nic*** complexes were each sprayed simultaneously with an equal concentration and equal volume of control porphyrin in order for each species to experience identical instrumental conditions. The MS parameters used for the experiments (positive-ion mode) were as follows: capillary voltage, 1.5 kV; sample cone, 150 V; extractor cone, 0 V; ion transfer stage pressure (monitored by a Pirani gauge), 2.0−2.5 mbar; TOF analyzer pressure (monitored by a Penning gauge), $(4.0-4.5) \times 10^{-7}$ mbar. External calibration of the spectra and calibration of the LCT mass spectrometer were achieved using a 100 mg mL^{-1} solution of cesium iodide. Data were acquired and processed with MassLynx 4.0 software (Waters, Manchester, U.K.). All spectra are shown with minimal smoothing and without background subtraction.

Crystal Structure Determinations. A Bruker Apex II diffractometer on Station 9.8, at SRS, CCLRC Daresbury Laboratory, synchrotron radiation $\lambda = 0.6904$ Å, equipped with an Oxford Cryostream crystal cooling apparatus (silicon 111 monochromator, ω scans), was used. X-ray data were recorded at 123 K and corrected for absorption using *APEX2*.[11] The structures were solved by direct methods using *SIR2004*[12] and refined by full-matrix least squares using *SHELXL*.[13] The ordered atoms in each structure were refined with anisotropic displacement parameters, while the hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atom. In each structure, the butyl groups associated with the porphyrins and chloroform, dichloromethane, or hexane solvent molecules showed extensive disorder, and in the majority of cases, these were refined isotropically, with disorder modeled over two sites with the sum of the occupancies fixed at unity and restraints applied to the bond parameters. Crystal data for **1-*Isonic***: $M = 2175.06$ g mol^{-1}, monoclinic $P2_1/c$ (No. 14), $a = 16.4641(11)$ Å, $b = 30.555(2)$ Å, $c = 35.228(2)$ Å, $\beta = 90.01(1)°$, $V = 17722(2)$ Å^3, $Z = 4$, $\mu = 0.175$ mm^{-1}, 65 054 reflections measured, 18 229 independent reflections, R1 = 0.140, wR2 = 0.391 for all data. Crystal data for **1-*Nic***: $M = 1429.36$ g mol^{-1}, monoclinic $P2_1/c$ (No. 14), $a = 19.6254(11)$ Å, $b = 27.6834(15)$ Å, $c = 16.7274(9)$ Å, $\beta = 91.590(1)°$, $V = 9084.5(9)$ Å^3, $Z = 4$, $\mu = 0.113$ mm^{-1}, 68 119 reflections measured, 15 398 independent reflections, R1 = 0.125, wR2 = 0.440 for all data.

Synthesis of Complex 1-*Isonic*. To a solution of tetrakis(3,5-di-*tert*-butylphenyl)porphyrinatoaluminum(III) hydroxide (**1-*OH***; 0.050 g, 0.045 mmol) in 10 mL of $CHCl_3$ was added, as a solid, 5 equiv of isonicotinic acid (0.027 g, 0.226 mmol). The resulting solution was stirred at room temperature for 12 h, at which time it was filtered to remove excess isonicotinic acid. The dark-purple filtrate was evaporated, yielding **1-*Isonic*** as a purple solid (0.049 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): 9.02 (s, 8H, $H_{\beta_{pyrrole}}$), 7.95−7.87 (br m, 8H, H_a), 7.77 (t, 4H, $J = 1.8$ Hz, H_b), 6.65 (br s, 2H, $H_{\alpha_{pyr}}$), 4.62 (br s, 2H, $H_{\beta_{pyr}}$), 1.47 (br s, 72H, $H_{3,5\text{-}tert\text{-butyl}}$). UV/vis ($CH_2Cl_2$): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 418 (4.9×10^5), 548 (1.8×10^4). MALDI-MS (calcd) for $C_{82}H_{96}AlN_5O_2$: [M]$^+$ m/z 1209.73. Found: m/z 1209.54.

Synthesis of Complex 1-*Nic*. To a solution of tetrakis(3,5-di-*tert*-butylphenyl)porphyrinatoaluminum(III) hydroxide (**1-*OH***; 0.050 g, 0.045 mmol) in 10 mL of $CHCl_3$ was added, as a solid, 5 equiv of nicotinic acid (0.027 g, 0.226 mmol). The resulting solution was

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stirred at room temperature for 12 h,t which time it was filtered to remove excess isonicotinic acid. The dark-purple filtrate was evaporated, yielding **1-*Nic*** as a purple solid (0.047 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): 9.06 (s, 8H, $H_{\beta_{pyrrole}}$), 8.02−7.92 (br d, 8H, H_a), 7.77 (t, 4H, $J = 1.7$ Hz, H_b), 7.24 (br s, 1H, $H_{\alpha_{pyr}}$), 6.34 (br s, 1H, $H_{\beta_{pyr}}$), 6.14 (br s, 1H, $H_{\omega_{pyr}}$), 5.37 (br s, 1H, $H_{\gamma_{pyr}}$), 1.48 (br s, 72H, $H_{3,5\text{-}tert\text{-butyl}}$). UV/vis ($CH_2Cl_2$): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 418 (5.0×10^5), 548 (1.9×10^4). MALDI-MS (calcd) for $C_{82}H_{96}AlN_5O_2$: $[M]^+$ *m/z* 1209.73. Found: *m/z* 1209.51.

Acknowledgment. We thank EPSRC and NSERC (G.J.E.D.) for financial support.

Supporting Information Available: X-ray crystallographic data in CIF format and ^{1}H NMR and MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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