Porphyrins with Exocyclic Rings. 15.[1] Synthesis of Quino- and Isoquinoporphyrins, Aza Analogues of the Naphthoporphyrins

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Porphyrins with fused isoquinoline and quinoline units have been prepared by the "3 + 1" methodology. 5-Nitroisoquinoline and 6-nitroquinoline condensed with ethyl isocyanoacetate in the presence of a phosphazene base to give isoquino- and quinopyrroles, respectively. Ester saponification and decarboxylation with KOH in ethylene glycol at 190 °C gave the parent azatricycles, and these were further condensed with 2 equiv of an acetoxymethylpyrrole to give the corresponding tripyrranes protected at the terminal positions as their *tert*-butyl esters. In a one-pot procedure, the ester protective groups were cleaved with TFA, and following dilution with dichloromethane, "3 + 1" condensation with a pyrrole dialdehyde and dehydrogenation of the phlorin intermediate with DDQ gave the targeted azanaphthoporphyrins in excellent yields. Although the UV−vis spectra of these new porphyrin systems are unexceptional, they show promise for further functionalization and applications in the development of porphyrin arrays. In addition, a zinc chelate of the isoquinoporphyrin system shows a high degree of regioselective intermolecular interaction/aggregation in chloroform solution that may lead to selectivity in molecular recognition studies.

Introduction

Porphyrins with fused aromatic rings had been little investigated until fairly recently,[2] with the notable exception of the benzoporphyrins and other structural analogues of the phthalocyanines.[2−4] Our initial interest in this area[5] was spurred by the presence of monobenzoporphyrins in petroleum,[6−9] tetrapyrrolic compounds of unknown origin, and by speculation on the geological occurrence of more highly condensed structures such as naphthoporphyrins.[9,10] Extension of the porphyrin chromophore offers the possibility of shifting the major UV−vis absorptions to higher wavelengths, a particularly valuable feature that could have wide ranging applications including the development of novel optical materials[11] and the production of new photosensitizers for medicinal applications.[12] In addition, alteration of the dimensions of these planar conjugated structures could have value by providing a platform for the design of unique molecular recognition systems.

Our early investigations were directed toward naphtho[1,2-*b*]porphyrins **1**[9,13,14] and phenanthroporphyrins **2** (Chart 1),[15] and efficient methodologies were developed

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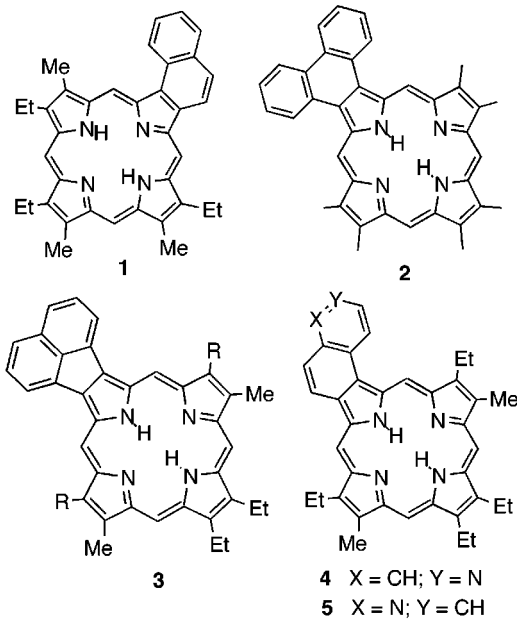
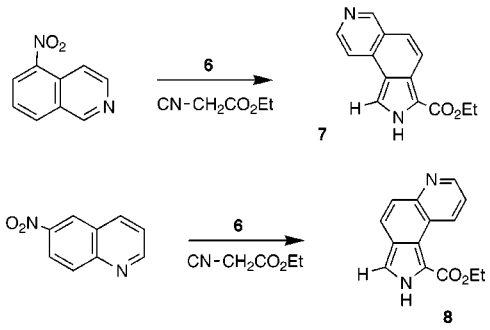
Chart 1. Porphyrins with Fused Aromatic Subunits



for the synthesis of structures of this type.[2,9,13−22] Surprisingly, fused naphthalene and phenanthrene rings had only a minor effect on the porphyrin chromophore.[9,13−15] For instance, phenanthroporphyrin **2** shows a bathochromic shift to the longest wavelength Q-band of approximately 10 nm while the Soret band is shifted by less than 20 nm compared to typical octaalkylporphyrins.[15] While naphthalene and phenanthrene rings produced very minor effects, acenaphthoporphyrins (e.g., **3**, Chart 1) were subsequently shown to produce major red shifts to all of the porphyrin absorption bands.[16] These studies were aided by the observation that certain nitroaromatic compounds reacted with isocyanoacetates in the presence of a nonnucleophilic base to give *c*-annelated pyrroles,[13−19,23] ideal intermediates for the synthesis of fused porphyrin structures such as **1**−**3**. In the present paper, we report the synthesis of porphyrins with fused isoquinoline **4** and quinoline rings **5** (Chart 1).[24] These

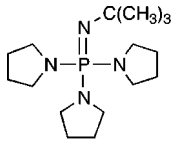
Scheme 1



structures are aza-analogues of the naphtho[1,2-*b*]porphyrins **1**, and it was of interest to see whether the presence of a heteroatom on the fused bicycle had any influence on the UV−vis spectra of the resulting porphyrins. More importantly, these units can easily be functionalized, particularly by quaternization of the external nitrogen, and this offers the possibility of both increasing the solubility of these new porphyrin systems and allowing the construction of linked or array structures that may be of value in the development of nanomolecular structures and in molecular recognition studies.

Results and Discussion

Recently, we reported[19] that 5-nitroisoquinoline and 6-nitroquinoline undergo "Barton−Zard" pyrrole condensations[25] with ethyl isocyanoacetate in the presence of the phosphazene base **6** to give isoquinopyrrole **7** and



6

quinopyrrole **8**, respectively (Scheme 1). In the earlier experiments, the reactions were carried out on a modest scale (approximately 200 mg of the nitroaromatic precursor), and on scale-up the yields were significantly improved, particularly in the case of isoquinopyrrole **7** where the yield of isolated product increased from 26% to 50%.[26] The physical properties of these isomeric tricycles were significantly different from one another, with **7** proving to be much more polar than **8** (R_f values on alumina plates developed with 20% ethyl acetate−toluene were 0.08 and 0.18 for **7** and **8**, respectively). Pyrrole esters are generally rather polar due to their doubly vinylogous carbamate character, as illustrated in Scheme 2, and it may be that the contribution from the dipolar resonance contributor **B** is reduced for **8** due to steric interactions. The proximity of an aromatic hydro-

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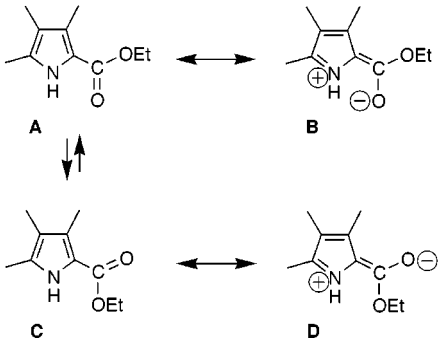
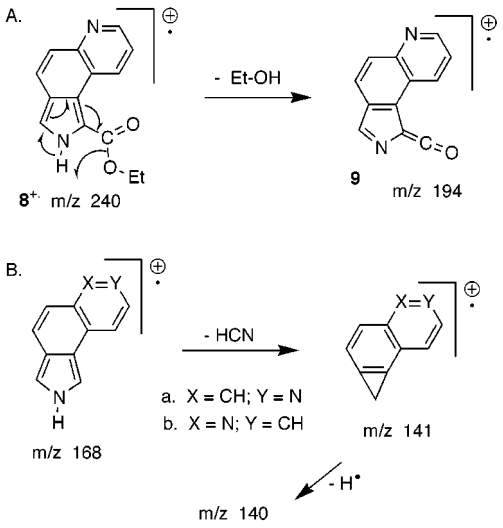
(26) 1-Nitronaphthopyrrole reacts with ethyl isocyanoacetate to give the corresponding naphthopyrrole in up to 65% yield at this scale, compared to a 33% isolated yield in the earlier work[19] (Manley, J. M.; Lash, T. D. Unpublished work).

Scheme 2



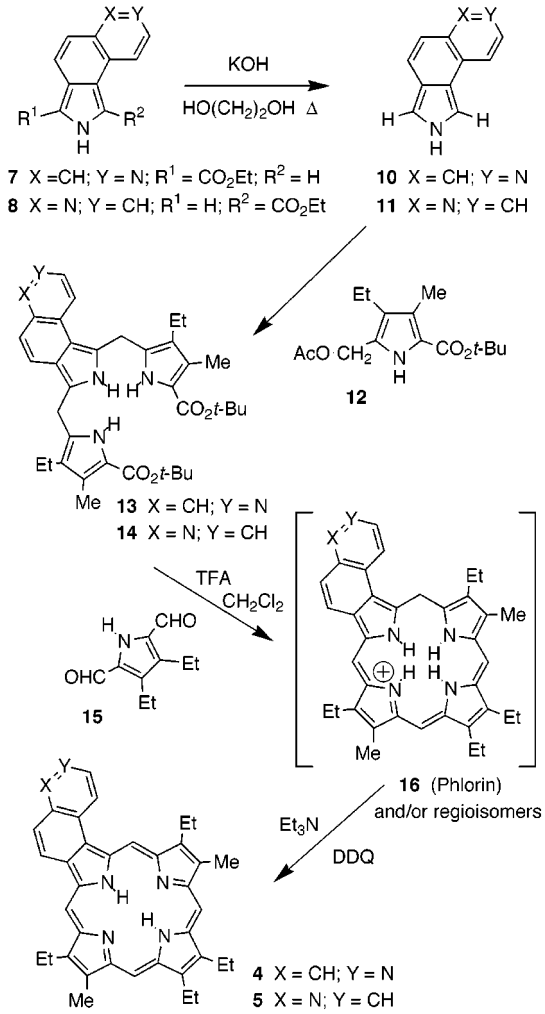
Scheme 3



gen to the carbonyl moiety is evident in the proton NMR spectrum of **8**, as a doublet is observed downfield at 10.1 ppm. In the infrared spectrum of quinopyrrole **8** the carbonyl resonance was observed at 1694 cm^{-1}, a value that is relatively high for a pyrrole ester of this kind. While this may indicate that the contribution from canonical form **B** is decreased relative to **A** (Scheme 2), the IR spectrum of **7** was more complex, showing the presence of two carbonyl bands at 1670 and 1690 cm^{-1}. These absorptions may be due to rotational conformers for the pyrrole ester (structures **A**/**B** vs **C**/**D** in Scheme 2). While these absorption bands are lower for pyrrole **7**, the difference in polarity between these pyrrole isomers may also be influenced by other factors such as hydrogen bonding interactions. Electron impact MS for both **7** and **8** show a strong molecular ion and a major fragment ion due to loss of ethanol presumably resulting from ketene cation radicals (e.g., structure **9**, Scheme 3A).

Cleavage of the ester units of **7** and **8** with KOH in ethylene glycol at 190 °C, in the presence of a small amount of hydrazine and under a nitrogen atmosphere, afforded good yields of the parent heterocycles **10** and **11** (Scheme 4). These showed intense molecular ions by electron impact MS and minor fragmentation due to loss of HCN (Scheme 3B). These pyrrolic precursors were now in a suitable form to construct the related isoquino- **4** and quinoporphyrins **5** using the "3 + 1" methodology. This approach (Scheme 4), which involves the condensation of a tripyrrane with a pyrroledialdehyde, was first used to prepare porphyrins by Boudif and Momenteau,[21,27] but we have independently designed related protocols which are particularly well suited for the synthesis

Scheme 4



of porphyrins with fused aromatic rings.[16,18,20−22,28] Condensation of **7** and **8** with 2 equiv of acetoxymethylpyrrole **12** in refluxing acetic acid/2-propanol afforded the modified tripyrranes **13** and **14**, respectively (Scheme 4). The mildly acidic conditions were compatible with the presence of *tert*-butyl protective groups and allowed a one-pot synthesis of the required azanaphthoporphyrins. Isoquinotripyrrane **13** was obtained in pure form after recrystallization from ethanol and fully characterized, but the related quinotripyrrane **14** was used in crude form. Treatment with TFA, followed by dilution with dichloromethane, addition of dialdehyde **15**, and oxidation with DDQ gave isoquinoporphyrin **4** and the quinoporphyrin **5** in 81 and 66% yields, respectively (Scheme 4). These exceptionally high yields demonstrate that this approach is particularly valuable in the synthesis of porphyrins with fused nitrogen heterocycles. Prior to the addition of DDQ, the reaction mixtures were a deep green color, and the UV−vis spectra showed a broad absorption near 740 nm. This is consistent with the intermediacy of phlorin intermediates **16** (Scheme 4), species that have previously been proposed as intermediates in "3 + 1" syntheses of this type.[22,29]

Both porphyrins were sparingly soluble in chloroform but gave clean ^1H NMR spectra in $CDCl_3$. The solubility

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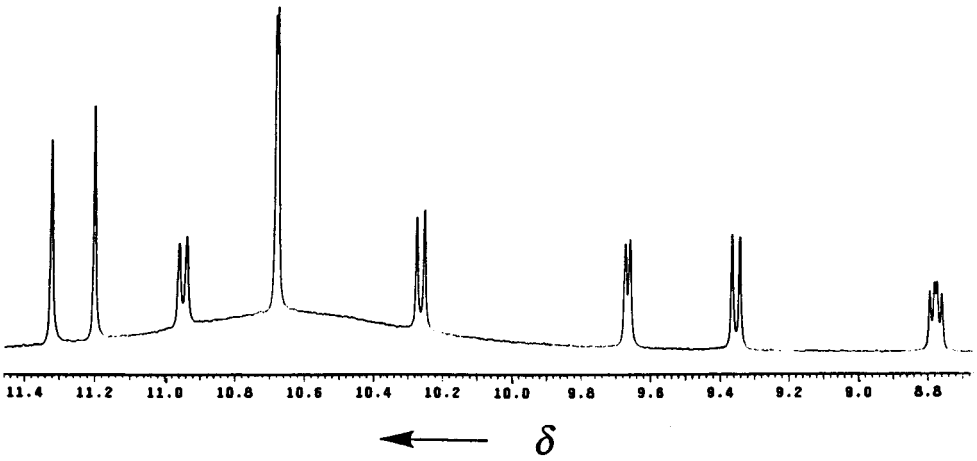


Figure 1. Downfield region of the 400 MHz proton NMR spectrum for quinoporphyrin **5** in TFA−$CDCl_3$. The broad absorption centered on 10.6 ppm is due to TFA.

was greatly increased upon addition of TFA, and this allowed the carbon-13 NMR spectra to be obtained as well. As crude tripyrrane was used to synthesize **5**, it was particularly important to demonstrate the isomeric purity of this porphyrin. The 400 MHz ^{1}H NMR spectrum for the protonated porphyrin (Figure 1) showed all four *meso*-protons (bridge methines) and five well-resolved signals for the quinoline protons. Carbon-13 NMR spectroscopy has been shown to be sensitive to the presence of porphyrin isomers and provides a useful tool in assessing structures of this type. At 100 MHz, quinoporphyrin **5** showed 26 of the 27 expected sp^2 carbon resonances, and 9 of the 10 anticipated sp^3 carbon resonances, and in particular gave four signals for the four nonequivalent *meso*-carbons between 98 and 100.1 ppm. The structure was further confirmed by electron impact mass spectrometry. Isoquinoporphyrin **4** gave comparable high quality NMR and MS data.

The UV−vis spectra of **4** and **5** in chloroform (Figure 2) were unexceptional, showing intense Soret bands at 418 and 419 nm, respectively, and the Q-band region from 500 to 650 nm closely resembled the spectrum previously obtained for mononaphthoporphyrin **1**.[9,13] In 10% TFA−chloroform, the green protonated porphyrins gave red shifted and intensified Soret bands at 431 nm for isoquinoporphyrin **4** and 426 nm for quinoporphyrin **5**.

The nickel(II), copper(II), and zinc chelates **17a**−**c** and **18a**−**c** were prepared from the free base porphyrins and the corresponding metal acetates under standard conditions (Scheme 5). The zinc chelates showed considerable aggregation in solution (chloroform or 1% triethylamine−chloroform) with broadened Soret absorptions (Figure 3). Addition of pyrrolidine considerably increased the solubility of these metalloporphyrins, and the UV−vis absorption bands were sharpened and significantly red-

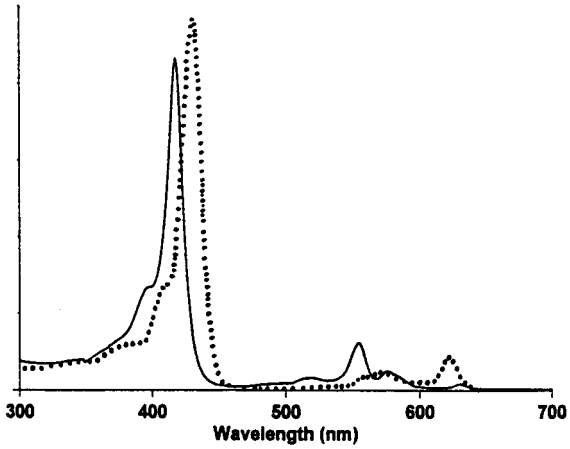
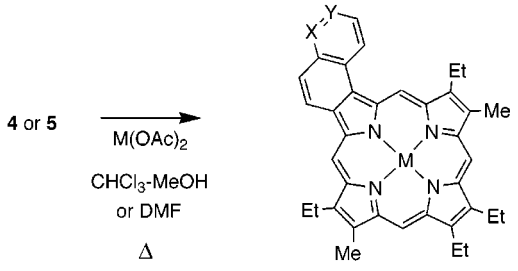


Figure 2. UV−vis spectra of isoquinooporphyrin **4**. Bold line: free base in chloroform. Dotted line: Protonated isoquinoporphyrin in 10% TFA−chloroform.

Scheme 5



shifted (Figure 3). Presumably pyrrolidine disrupts π-stacking interactions between individual molecules by hydrogen bonding interactions, although it has little effect on the spectra for the copper(II) or nickel(II) chelates. Taking this into account, it is clear that the absorption bands in both series shifted to longer wavelengths going from nickel to copper to zinc, i.e., across the periodic table, as has been observed previously for porphyrin systems.[2,30] For instance, in the isoquinoporphyrin series the nickel(II) complex **17a** gives a Soret

(28) This methodology has also proven to be exceptionally valuable in the synthesis of porphyrin analogues: Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533. Lash, T. D.; Chaney, S. T. *Tetrahedron Lett.* **1996**, *37*, 8825. Lash, T. D.; Chaney, S. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 839. Lash, T. D.; Hayes, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 839. Hayes, M. J.; Lash, T. D. *Chem. Eur. J.* **1998**, *4*, 508. Lash, T. D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076. Lash, T. D.; Richter, D. T. *J. Am. Chem. Soc.* **1998**, *120*, 9965. Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973. Lash, T. D. *Synlett* **2000**, 279.

(29) Burns, D. H.; Shi, D. C.; Lash, T. D. *Chem. Commun.* **2000**, 299.

(30) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; pp 871−889.

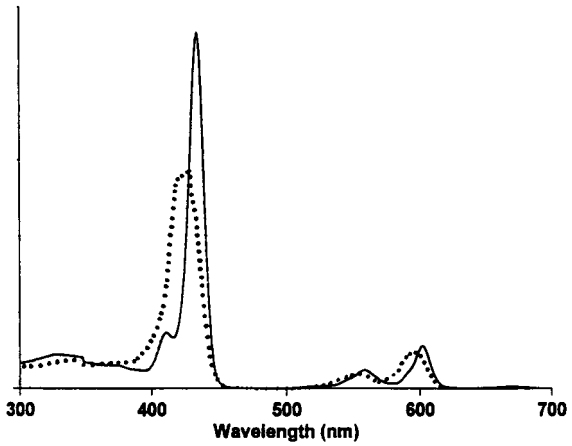


Figure 3. UV−vis spectra of isoquinoporphyrin zinc chelate **17c**. Dotted line: Aggregated complex in 1% triethylamine−chloroform. Bold line: Solution of **17c** in 1% pyrrolidine−chloroform.

band at 410 nm and its longest wavelength (α) band at 579 nm, while these absorptions appear at 415 and 586 nm for the copper(II) complex **17b** and 435 and 602 nm for the zinc complex **17c** in the presence of pyrrolidine.

The proton NMR spectra for the nickel(II) chelates **17a** and **18a** were well resolved and showed a small upfield shift to some of the resonances compared to the free base systems that suggests a decrease in the porphyrin ring current. For instance, the ring methyl groups appeared at 3.66 and 3.69 ppm in **4**, while the corresponding nickel-(II) complex **17a** gave values of 3.47 and 3.48 ppm for these units. The quinoporphyrin zinc complex **18c**, although sparingly soluble, gave a proton NMR spectrum that was consistent with the expected structure. However, three of the isoquinoline resonances for the zinc complex **17c** were broadened and shifted upfield, although the rest of the spectrum was in accord with expectations (Figure 4). Addition of a drop of pyrrolidine to the NMR tube sharpened up the spectrum, and the anomalous peaks were shifted downfield to give values similar to those observed for the free base porphyrin **4** (Figure 4). The data suggest that solutions of zinc chelate **17c** aggregate primarily at the isoquinoline rings as shown in Figure 5. This leads to three of the isoquinoline protons being shielded by the π-system of the associated metalloisoquinoporphyrin.[31] The regioselectivity of this interaction has the potential for application in molecular recognition studies.

Conclusion

The first examples of quino- and isoquinoporphyrins are reported. These were obtained in excellent overall yields from commercially available 6-nitroquinoline and 5-nitroisoquinoline by utilizing the Barton-Zard pyrrole synthesis and the MacDonald "3 + 1" methodology. The introduction of external heterocyclic units will allow the synthesis of water soluble quaternary salts and the production of linked array structures.

Experimental Section

Phosphazene base P_1-t-Bu-tris(tetramethylene) (**6**) was purchased from Fluka Chemie AG and was used without further purification. Chromatography was performed using

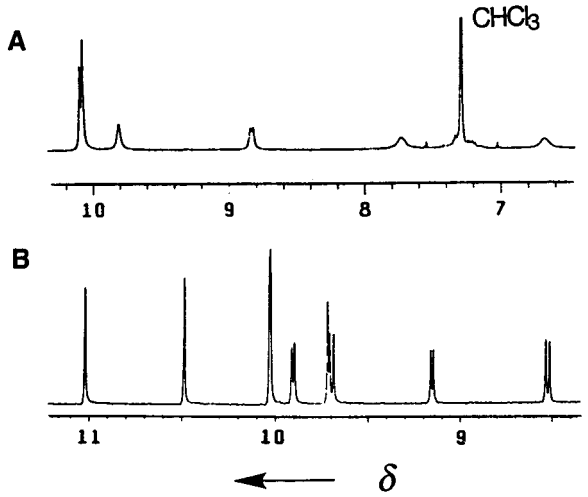


Figure 4. (A) Dowfield region for the 400 MHz proton NMR spectrum of zinc chelate **17c** in $CDCl_3$. Three of the isoquinoline proton resonances appear as broad upfield-shifted resonances between 6.6 and 7.8 ppm. The middle broad resonance overlaps with the residual chloroform peak at 7.3 ppm. (B) The downfield region for the same NMR solution after the addition of one drop of pyrrolidine. The deaggregated solution shows sharp well-resolved peaks, and the anomalous upfield resonances have returned to their expected higher field chemical shifts.

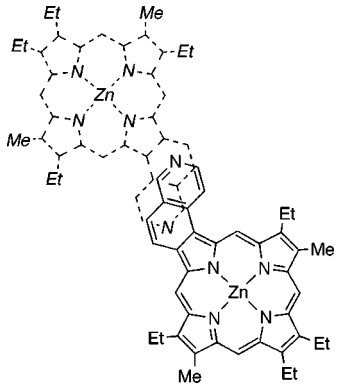


Figure 5. Proposed intermolecular interaction/aggregation of zinc isoquinoporphyrin **17c** in chloroform solution.

Grade 3 neutral alumina or 70−230 mesh silica gel. Metalloporphyrins were prepared under standard conditions by reacting the free base porphyrin with nickel(II), copper(II) or zinc acetate in methanol−chloroform[32] or DMF.[33] Melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus or a Mel-Temp apparatus and are uncorrected. EI and FAB mass spectral determinations were made at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana−Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029). Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

Ethyl Isoquino[5,6-*c*]pyrrole-3-carboxylate (7). Phosphazene base **6** (4.27 g) was added dropwise to a solution of ethyl isocyanoacetate[34] (2.00 g) and 5-nitroisoquinoline (2.32 g) in THF (100 mL; freshly distilled from calcium hydride),

(31) For a similar example, see: Lash, T. D.; Chaney, S. T. *Chem. Eur. J.* **1996**, *2*, 944.

(32) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; p 798.

(33) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(34) Hartman, G. D.; Weinstock, L. M. *Org. Synth.* **1979**, *59*, 183.

(35) Clezy, P. S.; Crowley, R. J.; Hai, T. T. *Aust. J. Chem.* **1982**, *35*, 411.

and the resulting mixture was stirred under reflux overnight. The solution was diluted with chloroform, washed with water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica, eluting with dichloromethane and then chloroform and finally 1% methanol−chloroform. Recrystallization from methanol afforded the isoquinopyrrole (1.61 g; 50%) as off-white crystals, mp 203 °C, dec; IR (Nujol mull): ν 3253 (NH str), 1690, 1670 cm^{-1} (C=O str); ^1H NMR ($CDCl_3$): δ 1.49 (3H, t, J = 7.2 Hz), 4.49 (2H, q, J = 7.2 Hz), 7.59 (1H, d, J = 9.2 Hz), 7.96−7.98 (2H, m), 8.15 (1H, d, J = 9.2 Hz), 8.64 (1H, br m), 9.13 (1H, s), 10.26 (1H, br s); ^1H NMR (d_6-DMSO): δ 1.42 (3H, t, J = 7.2 Hz), 4.41 (2H, q, J = 7.2 Hz), 7.66 (1H, d, J = 8.8 Hz), 8.09 (1H, d, J = 8.8 Hz), 8.26 (1H, d, J = 5.2 Hz), 8.42 (1H, d, J = 2.4 Hz), 8.60 (1H, d, J = 5.6 Hz), 9.14 (1H, s), 13.37 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 14.5, 59.7, 113.2, 116.6, 118.7, 119.1, 121.2, 123.7, 125.0, 125.4, 132.4, 145.0, 150.5, 160.5; MS (EI, 70 eV): m/z (%): 240 (83) [M^+], 194 (100) [M^+ − EtOH], 166 (36), 140 (28). Anal. Calcd for $C_{14}H_{12}N_2O_2 \cdot {}^1/_4H_2O$: C, 68.70; H, 5.15; N, 11.45. Found: C, 68.98; H, 4.93; N, 11.80.

Ethyl Quino[5,6-*c*]pyrrole-1-carboxylate (8). The title compound was prepared from 6-nitroquinoline by the previous procedure. The crude product was purified by chromatography on a Grade 3 alumina column eluting with dichloromethane. Recrystallization from toluene gave the quinopyrrole (1.69 g; 53%) as pale yellow microneedles, mp 180−181 °C; IR (Nujol mull): ν 1694 cm^{-1} (C=O str); ^1H NMR ($CDCl_3$): δ 1.46 (3H, t, J = 7.2 Hz), 4.48 (2H, q, J = 7.2 Hz), 7.49−7.54 (2H, m), 7.68 (1H, d, J = 9 Hz), 7.81 (1H, d, J = 9 Hz), 8.85 (1H, d, J = 3.6 Hz), 10.13 (1H, d, J = 8.4 Hz), 10.24 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 14.9, 61.0, 115.8, 116.5, 121.0, 123.6, 123.8, 124.1, 125.8, 136.0, 148.5, 149.6, 160.5; MS (EI, 70 eV): m/z (%): 240 (100) [M^+], 194 (95) [M^+ − EtOH], 166 (35), 140 (15), 118 (14). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.98; H, 5.04; N, 11.65. Found: C, 69.69; H, 5.05; N, 11.64.

Isoquino[5,6-*c*]pyrrole (10). Nitrogen gas was bubbled through a mixture of **7** (500 mg) and potassium hydroxide (1.00 g) in ethylene glycol (12 mL) for 10 min, 4 drops of hydrazine were added, and the resulting solution was stirred under reflux on a preheated oil bath at 195 °C under an atmosphere of nitrogen for a further 30 min. The mixture was poured into ice/water, and the resulting gray precipitate was collected by suction filtration, washed well with water, and dried under vacuum overnight. The pyrrole (296 mg; 83%) was obtained as a light gray powder, mp 202 °C, dec; IR (Nujol mull): ν 3130 cm^{-1} (NH str); ^1H NMR ($CDCl_3$): δ 7.27 (1H, d), 7.33 (1H, m), 7.60 (1H, d, J = 9.2 Hz), 7.77 (1H, s), 7.89 (1H, d, J = 5.6 Hz), 8.55 (1H, d, J = 5.6 Hz), 9.01 (1H, s), 9.44 (1H, br s); ^1H NMR (d_6-DMSO): δ 7.21 (1H, d, J = 8.8 Hz), 7.39 (1H, s), 7.60 (1H, d, J = 8.8 Hz), 7.99 (1H, s), 8.03 (1H, d, J = 5.6 Hz), 8.44 (1H, d, J = 5.6 Hz), 8.93 (1H, s), 12.31 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 111.4, 112.0, 116.7, 117.6, 118.8, 121.5, 122.3, 125.5, 133.4, 144.6, 150.1; MS (EI, 70 eV): m/z (%): 168 (100) [M^+], 141 (11) [M^+ − HCN], 140 (13). Anal. Calcd for $C_{11}H_8N_2 \cdot {}^1/_5H_2O$: C, 76.90; H, 4.92; N, 16.31. Found: C, 77.17; H, 4.59; N, 16.45.

Quino[5,6-*c*]pyrrole (11). The title compound was prepared from **8** (500 mg) by the previous procedure and isolated as a pale gray powder (265 mg; 77%), mp 186−188 °C, dec (darkens at 182 °C); ^1H NMR ($CDCl_3$): δ 7.32 (1H, t, J = 2.2 Hz), 7.35 (1H, dd, J = 7.8, 4.8 Hz), 7.45 (1H, d, J = 9.6 Hz), 7.68 (1H, m, J < 1 Hz), 7.74 (1H, d, J = 8.8 Hz), 8.37 (1H, dd, J = 8.2, 0.8 Hz), 8.73 (1H, dd, J = 4.4, 1.6 Hz), 9.27 (1H, br s); ^1H NMR (d_6-DMSO): δ 7.20 (1H, d, J = 9 Hz), 7.36−7.41 (2H, m), 7.70 (1H, d, J = 9 Hz), 7.89 (1H, m, J < 1 Hz), 8.52 (1H, d, J = 8.4 Hz), 8.57−8.60 (1H, m), 12.15 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 111.1, 111.4, 118.8, 120.4, 121.0, 122.7, 124.0, 124.9, 130.6, 146.6, 147.6; MS (EI, 70 eV): m/z (%): 168 (100) [M^+], 141 (19) [M^+ − HCN], 140 (17). Anal. Calcd for $C_{11}H_8N_2 \cdot {}^1/_5H_2O$: C, 76.90; H, 4.92; N, 16.31. Found: C, 76.86; H, 4.48; N, 16.51.

Bis-1,3-(5-*tert*-butoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)isoquino[5,6-*c*]pyrrole (13). Nitrogen was bubbled through a mixture of isoquinopyrrole **10** (200 mg) and acetoxymethylpyrrole **12**[35] (670 mg) in 2-propanol (12 mL) and acetic acid (2 mL) for 10 min. The mixture was refluxed while stirring under a nitrogen atmosphere for 16 h. The solution slowly darkened and turned a deep red color. The solution was evaporated under reduced pressure and recrystallized from ethanol to give the tripyrrane (488 mg; 67%) as a salmon pink powder, mp 214−215 °C; ^1H NMR ($CDCl_3$): δ 0.94 (3H, t), 0.97 (3H, t), 1.50 (9H, s), 1.51 (9H, s), 2.25 (3H, s), 2.28 (3H, s), 2.3−2.4 (4H, 2 overlapping quartets), 4.18 (2H, s), 4.46 (2H, s), 7.18 (1H, d, J = 9.2 Hz), 7.41 (1H, d, J = 9.2 Hz), 7.76 (1H, d, J = 5.2 Hz), 8.47 (1H, br s), 8.50 (1H, d, J = 5.2 Hz), 8.55 (2H, br s), 8.94 (1H, s); ^{13}C NMR ($CDCl_3$): δ 10.7, 10.8, 15.5, 15.7, 17.4 (2), 22.8, 25.8, 28.7 (2), 80.7 (2), 114.3, 117.1, 118.4, 119.4, 119.8, 120.1, 120.5, 120.8, 121.4, 124.4, 124.8, 126.3, 126.4, 126.9, 127.1, 128.5, 134.7, 145.1, 150.4, 161.5, 161.6; MS (EI, 70 eV): m/z (%): 610 (12) [M^+], 510 (40); HRMS (EI): Calcd for $C_{37}H_{46}N_4O_4$: 610.3519. Found: 610.3527. Anal. Calcd for $C_{37}H_{46}N_4O_4 \cdot {}^1/_2H_2O$: C, 71.70; H, 7.64; N, 9.04. Found: C, 71.71; H, 7.39; N, 8.84.

Bis-1,3-(5-*tert*-butoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)quino[5,6-*c*]pyrrole (14). Tripyrrane **14** was prepared by the previous procedure from **11** (200 mg) and **12** (670 mg). Trituration with hexanes gave the tripyrrane (530 mg, 73%) as an orange-yellow powder, mp 146−147 °C. Although this material was not pure by NMR, it was used without further purification. ^1H NMR ($CDCl_3$): δ 0.93−0.97 (6H, 2 overlapping triplets), 1.49 (9H, s), 1.50 (9H, s), 2.25 (3H, s), 2.27 (3H, s), 2.3−2.4 (2 overlapping quartets), 4.17 (2H, s), 4.59 (2H, s), 7.28 (1H, m), 7.35 (1H, d, J = 9 Hz), 7.53 (1H, d, J = 9 Hz), 8.18 (1H, d, J = 8 Hz), 8.45 (1H, br s), 8.55 (1H, br s), 8.64 (1H, d, J = 4.4 Hz), 8.68 (1H, br s); HRMS (EI): Calcd for $C_{37}H_{46}N_4O_4$: 610.3519. Found: 610.3519.

7,12,13,18-Tetraethyl-8,17-dimethylisoquino[5,6-*b*]porphyrin (4). Tripyrrane **13** (150 mg) was dissolved in TFA (2 mL) and stirred at room temperature for 10 min under nitrogen. The mixture was diluted with dichloromethane (38 mL), followed immediately by the addition of pyrroledialdehyde **15**[22] (44 mg). The mixture was stirred under nitrogen for a further 3 h. Then, the mixture was neutralized by the dropwise addition of triethylamine, DDQ (55 mg) was added, and the solution was stirred for another 1 h. The solution was then diluted with chloroform and washed with water, and the solvent was evaporated under reduced pressure. The residue was chromatographed on a Grade 3 alumina column, eluting with dichloromethane. Recrystallization from chloroform−methanol gave the isoquinoporphyrin (110 mg; 81%) as dark purple crystals, mp 290 °C, dec; UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 396 (sh), 418 (5.38), 519 (3.90), 554 (4.51), 576 (4.12), 630 nm (3.57); UV−vis (10% TFA-$CHCl_3$): λ_{max} (log ϵ) 408 (sh), 431 (5.43), 569 (4.11), 622 nm (4.37); ^1H NMR ($CDCl_3$): δ −3.99 (2H, br s), 1.88−1.95 (12H, m), 3.66 (3H, s), 3.69 (3H, s), 4.03 (4H, q, J = 7.8 Hz), 4.07−4.18 (4H, 2 overlapping quartets), 8.42 (1H, d, J = 8.3 Hz), 9.10 (1H, d, J = 6 Hz), 9.36 (1H, d, J = 8.8 Hz), 9.52 (1H, d, J = 6 Hz), 9.70 (1H, s), 10.03 (1H, s), 10.04 (1H, s), 10.28 (1H, s), 10.71 (1H, s); ^1H NMR (TFA−$CDCl_3$): δ −3.01 (2H, br s), −2.78 (1H, br s), −2.36 (1H, br s), 1.66−1.80 (12H, m), 3.67 (3H, s), 3.68 (3H, s), 4.12−4.25 (8H, 4 overlapping quartets), 9.27 (1H, d, J = 8.8 Hz), 9.54 (1H, d, J = 6.4 Hz), 10.07 (1H, d, J = 8.8 Hz), 10.27 (1H, d, J = 6.7 Hz), 10.54 (1H, s), 10.65 (1H, s), 10.67 (1H, s), 11.19 (1H, s), 11.32 (1H, s); ^{13}C NMR (TFA−$CDCl_3$): δ 12.1 (2), 16.4, 16.6, 17.5, 17.6, 20.2, 20.4 (2), 98.1, 98.5, 99.4, 100.1, 123.6, 124.4, 126.0, 129.4, 132.2, 135.3, 135.9, 137.5, 137.7, 138.2, 138.5, 138.6, 142.0, 142.7, 143.1, 143.6, 143.8, 144.4, 144.7, 145.0, 145.1, 147.6; MS (EI, 70 eV): m/z (%): 551 (6) [M^+], 536 (1); HRMS (EI): Calcd for $C_{37}H_{37}N_5$: 551.3049. Found: 551.3050. Anal. Calcd for $C_{37}H_{37}N_5 \cdot H_2O$: C, 78.00; H, 6.90; N, 12.29. Found: C, 78.28; H, 6.65; N, 12.09. Nickel(II) complex (**17a**): purple crystals, mp 275 °C, dec (chloroform−methanol); UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 410 (5.11), 534 (3.87), 579 nm (4.52); ^1H NMR ($CDCl_3$): δ 1.77−1.87 (12H, m), 3.47 (3H, s), 3.48 (3H, s), 3.9−4.0 (8H, m), 8.39 (1H, d, J = 8.4 Hz), 9.12 (1H, d, J = 5.6 Hz), 9.31 (1H, d, J = 8.0 Hz), 9.40 (1H, br d, J = 4.4 Hz), 9.70 (1H, s), 9.73 (1H, s), 9.74 (1H, s), 10.04 (1H, s), 10.53 (1H, s); HRMS (FAB): Calc. for $C_{37}H_{35}N_5Ni$ + H: 608.2324. Found: 608.2323. Copper(II) complex (**17b**): purple

crystals, mp > 300 °C, partial decomp at 280 °C (chloroform−methanol); UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 393 (sh), 415 (5.38), 541 (3.95), 586 nm (4.51); HRMS (FAB): Calc. for $C_{37}H_{35}N_5Cu$ + H: 613.2267. Found: 608.2264. Zinc complex (**17c**): dark green crystals, mp > 300 °C (chloroform−methanol); UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 428 (5.25), 554 (4.10), 596 (4.48), 669 nm (3.23); UV−vis (1% pyrrolidine-$CHCl_3$): λ_{max} (log ϵ) 412 (4.66), 435 (5.46), 558 (4.21), 602 (4.56), 672 nm (3.43); ^{1}H NMR ($CDCl_3$): δ 1.62 (3H, t), 1.86−1.96 (9H, m), 3.64 (3H, s), 3.69 (3H, s), 3.79 (2H, br q), 4.04−4.13 (6H, m), 6.64 (1H, br), 7.3 (1H, br), 7.75 (1H, br), 8.83 (1H, d, J = 8.0 Hz), 9.81 (1H, s), 10.08 (3H, s), 10.10 (1H, s); ^{1}H NMR (pyrrolidine−$CDCl_3$; downfield region only): δ 8.52 (1H, d, J = 8.8 Hz), 9.15 (1H, d, J = 6.0 Hz), 9.69 (1H, d, J = 8.8 Hz), 9.72 (1H, s), 9.90 (1H, d, J = 6.0 Hz), 10.02 (1H, s), 10.03 (1H, s), 10.49 (1H, s), 11.02 (1H, s); HRMS (FAB): Calcd for $C_{37}H_{35}N_5Zn$ + H: 614.2262. Found: 614.2259.

7,12,13,18-Tetraethyl-8,17-dimethylquino[5,6-*b*]porphyrin (5). Prepared from tripyrrane **14** (150 mg) and **15** (44 mg) by the previous procedure. Recrystallization from chloroform−methanol gave the quinoporphyrin (90 mg; 66%) as dark purple crystals, mp >300 °C; UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 399 (4.91), 419 (5.40), 518 (3.97), 554 (4.57), 575 (4.16), 630 nm (3.69); UV−vis (10% TFA-$CHCl_3$): λ_{max} (log ϵ) 388 (sh), 426 (5.25), 567 (4.17), 619 nm (4.43); ^{1}H NMR ($CDCl_3$): δ −3.92 (2H, br s), 1.91−1.95 (12H, m), 3.69 (3H, s), 3.70 (3H, s), 4.04 (4H, q, J = 7.3 Hz), 4.1−4.2 (4H, 2 overlapping quartets), 7.97 (1H, dd, J = 8.5, 4 Hz), 8.68 (1H, d, J = 8.3 Hz), 9.25 (1H, d, J = 3.4 Hz), 9.57 (1H, d, J = 8.3 Hz), 10.05 (1H, s), 10.06 (1H, s), 10.18 (1H, d, J = 8.3 Hz), 10.34 (1H, s), 10.71 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ −2.94 (2H, br s), −2.81 (1H, br s), −2.26 (1H, br s), 1.66 (3H, t, J = 7.6 Hz), 1.71−1.79 (9H, m), 3.65 (3H, s), 3.68 (3H, s), 4.11−4.24 (8H, m), 8.74 (1H, dd, J = 8.2, 5.5 Hz), 9.38 (1H, d, J = 9.1 Hz), 9.69 (1H, d, J = 4.9 Hz), 10.21 (1H, d, J = 9.1 Hz), 10.64 (2H, s), 10.89 (1H, d, J = 8.5 Hz), 11.15 (1H, s), 11.27 (1H, s); ^{13}C NMR (TFA−$CDCl_3$): δ 12.0, 12.1, 16.4, 16.6, 17.5, 17.6, 20.2, 20.4 (2), 97.8, 98.6, 99.5, 99.7, 124.6, 125.4, 126.4, 130.0, 133.9, 135.8, 137.0, 138.3, 138.4, 141.2 (2), 142.3, 142.5, 142.9, 143.2, 143.8, 144.0, 144.3 (2), 144.5, 144.6, 145.0; MS (EI, 70 eV): m/z (%): 551 (33) [M^+], 536 (5); HRMS (EI): Calcd for $C_{37}H_{37}N_5$: 551.3049. Found: 551.3046. Anal. Calcd for $C_{37}H_{37}N_5 \cdot {}^1/_4H_2O$: C, 79.89; H, 6.79; N, 12.59. Found: C, 79.78; H, 6.68; N, 12.49. Nickel(II) complex (**18a**): purple crystals, mp 240 °C, dec (chloroform−methanol); UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 412 (5.14), 533 (4.00), 578 nm (4.62); ^{1}H NMR ($CDCl_3$): δ 1.75−1.84 (12H, m), 3.45 (3H, s), 3.46 (3H, s), 3.88−3.96 (8H, m), 7.94 (1H, dd, J = 8.4, 4 Hz), 8.59 (1H, d, J = 7.6 Hz), 9.22 (1H, d, J = 3.2 Hz), 9.45 (1H, d, J = 8.8 Hz), 9.71 (2H, s), 9.56 (1H, d, J = 8.4 Hz), 10.03 (1H, s), 10.44 (1H, s); HRMS (FAB): Calc. for $C_{37}H_{35}N_5Ni$ + H: 608.2324. Found: 608.2323. Copper(II) complex (**18b**): dark purple crystals, mp 280 °C, dec (chloroform−methanol); UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 416 (5.30), 540 (4.02), 585 nm (4.56); HRMS (FAB): Calcd for $C_{37}H_{35}N_5Cu$ + H: 613.2267. Found: 613.2264. Zinc complex (**18c**): small purple crystals, mp > 300 °C (chloroform−methanol); UV−vis (1% E_3N−$CHCl_3$): λ_{max} (log ϵ) 423 (5.20), 551 (4.07), 592 (4.49), 665 nm (3.30); UV−vis (1% pyrrolidine−$CHCl_3$): λ_{max} (log ϵ) 415 (sh), 437 (5.31), 558 (4.18), 601 (4.51), 668 nm (3.47); ^{1}H NMR ($CDCl_3$): δ 1.66 (3H, t), 1.74 (3H, t), 1.87−1.93 (6H, 2 overlapping triplets), 3.32 (3H, s), 3.43 (3H, s), 3.59 (2H, br q), 3.78 (2H, q), 4.00 (4H, 2 overlapping quartets), 7.96 (1H, dd, J = 8.0, 4 Hz), 8.57 (1H, d, J = 8.8 Hz), 9.24 (1H, d, J = 3.2 Hz), 9.27 (1H, d, J = 8.0 Hz), 9.58 (2H, s), 9.69 (1H, s), 9.74 (1H, s), 9.78 (1H, d, J = 8.0 Hz); ^{1}H NMR (pyrrolidine−$CDCl_3$; downfield region only): δ 8.02 (1H, dd, J = 8.2, 4.2 Hz), 8.70 (1H, d, J = 8.8 Hz), 9.23 (1H, d, J = 3 Hz), 9.81 (1H, d, J = 8.4 Hz), 10.03 (1H, s), 10.04 (1H, s), 10.49 (1H, s), 10.52 (1H, d, J = 8.4 Hz), 10.96 (1H, s); HRMS (FAB): Calc. for $C_{37}H_{35}N_5Zn$ + H: 614.2262. Found: 614.2259.

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Supporting Information Available: Copies of UV−vis spectra for porphyrins **4** and **5**, and their nickel(II), copper(II), and zinc chelates, and ^{1}H NMR and selected ^{13}C NMR and EI mass spectra for compounds **4**, **5**, **7**, **8**, **10**, **11**, **13**, **14**, **17a**, **17c**, **18a**, and **18c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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