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Nitrogen Heterocyclic Carbon-Rich Materials: Synthesis and Spectroscopic Properties of Dehydropyridoannulene Macrocycles

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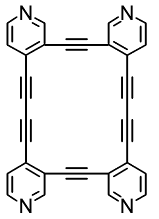

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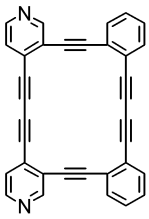

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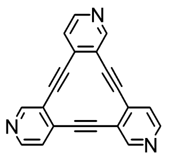

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A new series of nitrogen heterocyclic dehydroannulenes **1**−**3** have been synthesized and their macrocyclic structures assigned using spectroscopic methods. The chiral and planar ground state conformations of **1** and **3**, respectively, were determined by semiempirical theoretical calculations. All dehydropyridoannulenes and precursors possessing four aromatic rings functioned as fluorescent chromophores. A detailed spectroscopic investigation into the cation-binding properties of **3** in dilute solution revealed a particularly selective photoluminescence quenching sensory response for Pd^{II} ions. Cycle **3**, as well as **1** and **2**, also exhibited reversible proton-triggered luminescence quenching behavior. At higher concentrations, **3** afforded a coordination polymer precipitate with Ag^{I} ions. Cycles **1** and **2** and precursors **15**, **23**, and **29** also undergo thermochemical reactions that may potentially lead to carbon-rich polymers. The physicochemical properties of **1**−**3** suggest that dehydropyridoannulenes may serve as a particularly versatile new class of ligands for the creation of novel heteroatom-containing carbon-rich materials with many potential applications in supramolecular materials science and nanotechnology.

Introduction

Since the discovery of buckminsterfullerenes and carbon nanotubes, the synthesis and study of carbon-rich organic materials has rapidly spread into a domain of major scientific importance within the physical and chemical community.[1a−g] However, expanded carbon network polymers, which have been theoretically predicted to possess many intriguing mechanical and physicochemical properties, have so far eluded all attempts at preparation due to the formidable synthetic challenge of generating a defect-free lattice using conventional covalent bond chemistry.[2a−k] On the other hand, the preparation of ethynyl macrocycles which may serve as precursors to hypothetical carbon-rich polymer networks has been very productive as a result of their ready synthetic accessibility.[1a−e,g,2b,c,f,h,3a−f]

Of historical note, early reports in this field concentrated on the chemistry of dehydroannulene macrocycles,[4]

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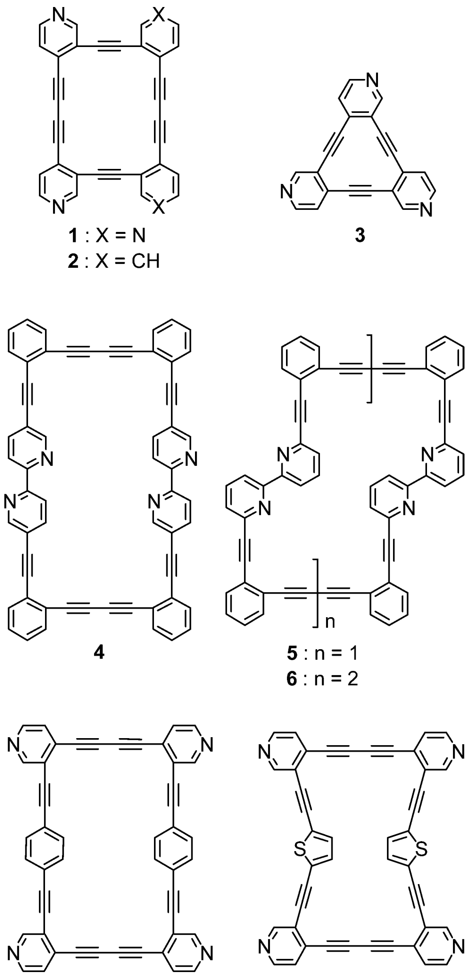
10.1021/jo040276f CCC: $30.25

which rapidly diversified in parallel to that of the structurally related annulenes, to encompass a wide range of cyclic conjugated hydrocarbons. These systems found use as model systems for the experimental verification of aromaticity and Hückel theory.[5a–c] In particular, dehydrobenzoannulenes are currently the focus of a surge in interest as they offer potential for structural elaboration into model sections of expanded carbon networks which include graphyne and graphdiyne.[3d–e,6a–e] Such cyclophanes have recently been demonstrated to exhibit NLO,[7] photochromic,[8] and high-spin magnetic behavior,[9] as well as serving as precursors for the generation of carbon buckyonions and nanotubes,[10a–d] and as interesting novel strained-ring systems.[11a–e] In the area of supramolecular chemistry, they have been reported to function as assembly units for the generation of pseudorotaxane-type architectures.[12]

An alternative to the covalent approach for the construction of network polymers based on dehydroannulene subunits would be to use supramolecular chemistry and, in particular, metal ion-induced autoassembly. In the latter situation, the mechanism of polymer formation will be expected to occur via reversible metal ion–ligand interactions in which errors are removed during growth of the network. Polymers of this type may topologically mimic those of the theoretically proposed carbon-rich nets, but with the additional feature that they would incorporate metal ions as integral structural units. Materials of this type would be especially interesting in that they may be expected to display a rich variety of exploitable properties such as electrochemical, photochemical, magnetic, optical, catalytic, porous, sensory, and mechanical behavior.[13a–d] With the aforementioned considerations as one of our goals, we have been developing a new class of heterocyclic dehydroannulene-type cyclophanes over the past years that incorporates pyridine rings as sites for metal ion complexation.[14a–r] These investigations demonstrated that cycles **4**–**8** (Chart 1) were strongly fluorescent chromophores affording characteristic photoluminescence sensory output responses in the presence of particular metal ions.

CHART 1



The present report discloses studies conducted in parallel to those detailed above and dealing specifically with the syntheses and spectroscopic properties of dehydroannulene macrocycles **1**–**3** (Chart 1). The preparation of building blocks for the construction of related, isomeric systems is also described, along with investigations into the photoluminescence and thermal properties of the macrocycles as well as the sensory behavior and coordination potential of **3** toward metal ions. The aromatic rings within **1**–**3** are all *ortho*-connected, and may therefore be regarded as true dehydropyridoannulenes.[5a,6c,15]

Results and Discussion

The syntheses of macrocycles **1**–**3** are shown in Schemes 1–4. The most efficient general method of

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(7) Sarkar, A.; Pak, J. J.; Rayfield, G. W.; Haley, M. M. *J. Mater. Chem.* **2001**, *11*, 2943.

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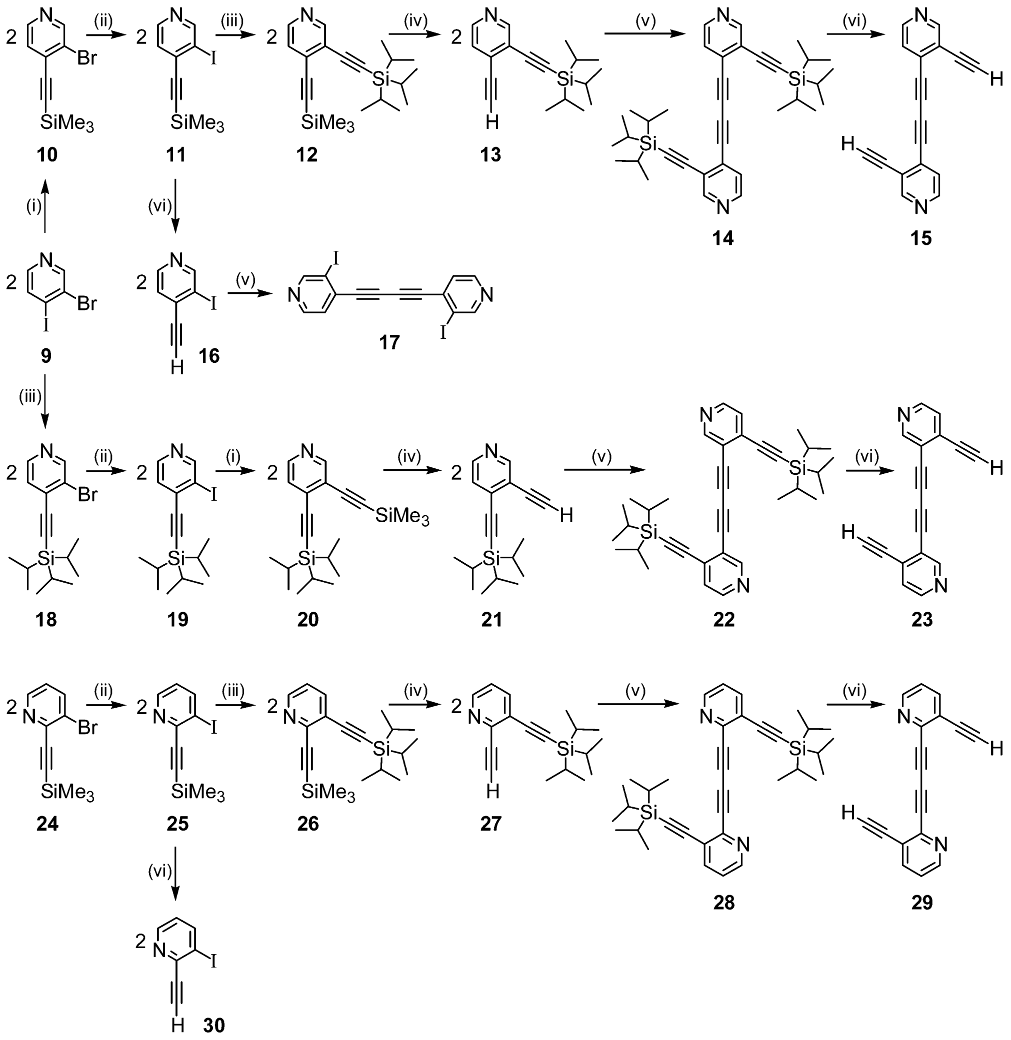
(11) For some recent examples of strained dehydrobenzoannulene ring systems, see: (a) Tobe, Y.; Ohki, I.; Sonoda, M.; Niino, H.; Sato, T.; Wakabayashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 5614. (b) Boydston, A. J.; Laskoski, M.; Bunz, U. H. F.; Haley, M. M. *Synlett* **2002**, 981. (c) Mitzel, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Diederich, F. *Chem. Commun.* **2002**, 2318. (d) Gallagher, M. E.; Anthony, J. E. *Tetrahedron Lett.* **2001**, *42*, 7533. (e) Bunz, U. H. F.; Enkelmann, V. *Chem. Eur. J.* **1999**, *5*, 263.

(12) Pak, J. J.; Weakley, T. J. R.; Haley, M. M.; Lau, D. Y. K.; Stoddart, J. F. *Synthesis* **2002**, 1256.

(13) The metal ion directed assembly of coordination polymer networks has been the subject of considerable effort. For recent reviews, see: (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Férey, G. *Chem. Mater.* **2001**, *13*, 3084. (c) Hosseini, M. W. In *Crystal Engineering: From Molecules and Crystals to Materials*; Braga, D., Grepioni, F., Orpen, G. A., Eds.; Kluwer: Dordrecht, 1999, pp 181–208. For an example of a three-dimensional coordination polymer incorporating ethynylpyridyl-type ligands, see: (d) Maekawa, M.; Konaka, H.; Suenaga, Y.; Kuroda-Sowa, T.; Munakata, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4160.

SCHEME 1. Synthesis of *o*-Diethynylpyridine Precursors[a]



[a] Key: (i) TMSA, $PdCl_2(PPh_3)_2$, CuI cat., Et_3N, 20 °C, 5−7 d {**10** (91%),[14c] **20** (96%)}; (ii) *n*-BuLi, Et_2O, −78 °C, 1.5 h, then ICH_2CH_2I/Et_2O, −78 °C, 3 h {**11** (86%),[14c] **19** (80%), **25** (93%)}; (iii) TIPSA, $PdCl_2(PPh_3)_2$, CuI cat., Et_3N, 20 °C, 5−7 d {**12** (96%), **18** (87%); 75 °C, 3 d: **26** (64%)}; (iv) K_2CO_3, MeOH, 20 °C, 17−36h {**13** (90%), **21** (99%), **27** (99%)}; (v) CuI or CuCl cat., O_2, pyridine, 20 °C, 18−48 h {**14** (86%), **17** (79%), **22** (68%), **28** (65%)}; (vi) 1 M $[(n\text{-Bu})_4N]F$, THF/H_2O, 20 °C, 14−36 h {**15** (76%), **16** (91%), **23** (96%), **29** (65%), **30** (76%)}.

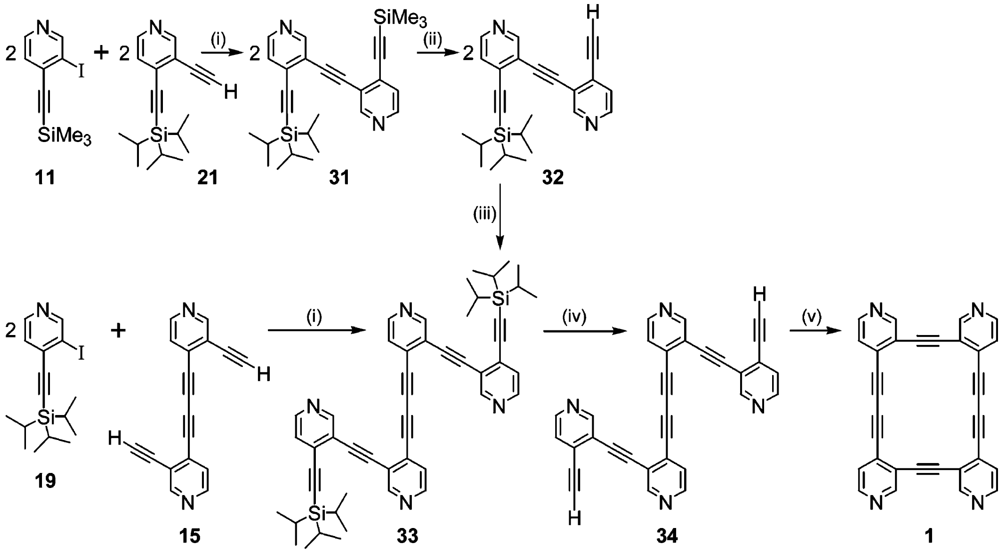
preparation of **1** and **2** utilized the pivotal monoprotected diethynylpyridine **21**, which was homologated via successive Sonogashira coupling, selective desilylation, and Hay coupling to afford tetraaryl precursors **33** and **38**. Further deprotection followed by copper-mediated intramolecular cyclizations yielded **1** and **2** (Schemes 1−3). Cycle **3** was obtained in low yield using the Stephens−Castro intermolecular organocuprate cyclotrimerization protocol (Scheme 4).

Synthesis of Dehydropyridoannulene Precursors 12−30. Unlike their dehydrobenzoannulene analogues, dehydropyridoannulenes such as **1**−**3** and related systems may exist as a range of isomers depending upon the relative positions of the pyridine nitrogens. Isomeric dehydropyridoannulenes are interesting synthetic targets as they will be expected to exhibit differing coordination arrangements as well as spectroscopic and electrochemical properties. For example, the study of structure/property relationships within a given library of isomeric dehydropyridoannulenes may enable optimization of the system for a particular function.[16] To obtain facile access to isomeric dehydropyridoannulenes, a modular series of *o*-diethynylpyridine building blocks were initially prepared (Scheme 1), the syntheses of which are described below.[17a−c]

Initial synthetic work revealed that 3-bromo-4-iodopyridine (**9**)[14c−18a−c] served as an ideal starting substrate for the construction of the 3,4-diethynylpyridyl subunits. Thus, **9** was converted via **10** to **11** as described in an earlier paper.[14c] The Sonogashira[19] reaction of **11** with TIPSA in Et_3N with $PdCl_2(PPh_3)_2$ and CuI catalysts afforded the *o*-diethynylpyridine **12** in 96% yield. Selective desilylation of **12** with K_2CO_3 in MeOH proceded cleanly to give **13** in 90% yield.[20] Dipyridine **14** was obtained in 86% yield from the Hay coupling[21a−c] of **13** in oxygenated pyridine solution with CuI catalyst. Deprotection of **14** with $[(n\text{-Bu})_4N]F$ in THF provided the particularly heat- and light-sensitive dehydropyridoannulene precursor **15** in 76% yield after workup.

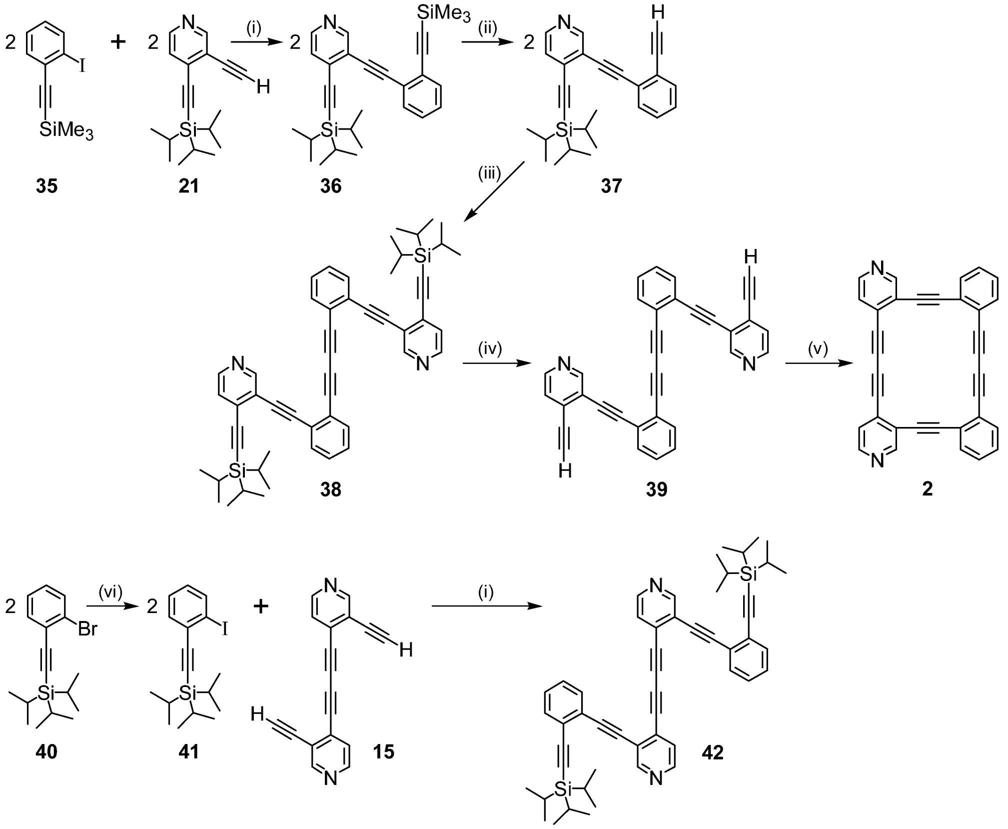
In an alternative route to **15**, iodopyridine **11** was deprotected with $[(n\text{-Bu})_4N]F$ in THF to give **16** in 91% yield and the latter coupled to afford **17** in 79% using CuCl in oxygenated pyridine. However, the Sonogashira reaction of **17** with TMSA in toluene/Et_3N provided the

SCHEME 2. Synthesis of Dehydrotetrapyrido[20]annulene 1[a]



[a] Key: (i) $PdCl_2(PPh_3)_2$, CuI cat. Et_3N, 20 °C, 5 d: **31** (75%); [$PdCl_2$(dppf)].CH_2Cl_2, CuI cat. toluene/Et_3N, 60 °C, 22 h: **33** (48%); (ii) K_2CO_3, MeOH, 20 °C, 20 h (91%); (iii) CuCl cat., O_2, pyridine, 20 °C, 24 h (77%); (iv) 1 M [(*n*-Bu)$_4$N]F, THF, H_2O, 20 °C, 20 h (99%); (v) [$Cu_2(OAc)_4$]·$2H_2O$, pyridine, 20 °C, 21 d (40%).

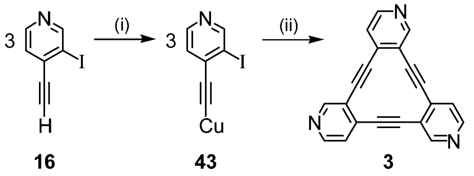
SCHEME 3. Synthesis of Dehydrodibenzodipyrido[20]annulene 2[a]



[a] Key: (i) CuI cat., toluene/Et_3N {$PdCl_2(PPh_3)_2$ cat., 20 °C, 6 d: **36** (77%); [$PdCl_2$(dppf)]·CH_2Cl_2 cat., 60 °C, 24 h: **42** (48%)}; (ii) K_2CO_3, MeOH, 20 °C, 36 h (88%); (iii) CuCl cat., O_2, pyridine, 20 °C, 48 h (94%); (iv) [(*n*-Bu)$_4$N]F, THF, H_2O, 20 °C, 24 h (91%); (v) $Cu_2(OAc)_4$, pyridine, 20 °C, 25 d (79%); (vi) *n*-BuLi, Et_2O, −78 to 0 °C, 1.2 h, then ICH_2CH_2I/Et_2O, −78 °C, 3 h (82%).

bis-trimethylsilyl analogue of **14** in only moderate yield and accompanied by contaminants that could not be removed by conventional column chromatography. This may in part be due to the poor solubility of **17** and the heat sensitivity of the desired reaction product. It may be noted that **14** was stable to heat, in stark comparison to **15**, and could be stored indefinitely at ambient temperature in the dark without any visible decomposition, highlighting the sterically stabilizing effect of the TIPS substituents.

SCHEME 4. Synthesis of Dehydrotripyrido[12]annulene 3[a]



[a] Key: (i) $CuSO_4{\cdot}5H_2O$, aq NH_3, $NH_2OH.HCl$, EtOH (95%); (ii) pyridine, 145 °C, 18 h (5%).

To prepare the isomeric dehydropyridoannulene precursor **23**, iodopyridine **9** was first converted to **18** in 87% yield, using conditions identical to those for the synthesis of **12** from **11**. Ethynylpyridine **18** was then lithiated at low temperature with *n*-BuLi in Et_2O and cleanly iodinated with ICH_2CH_2I to **19** in 80% yield. The reaction between **19** and TMSA in Et_3N with $PdCl_2(PPh_3)_2$ and CuI catalysts afforded **20** in 96% yield. The latter reaction sequence was performed in an analogous way to that of the indirect synthesis of **12** from **10** via **11**, as the more reactive iodopyridine **11** was found to be a superior coupling partner. Earlier attempts at the direct ethynylation of **10** using standard Sonogashira conditions resulted in products of inferior purity and lower yields.

Diethynylpyridine **20** was then selectively desilylated to **21** in 99% yield using conditions similar to those employed for the generation of **13**. The Hay coupling of **21** in oxygenated pyridine with CuCl provided the heat stable **22** in 68% yield, which was subsequently deprotected in an identical way to that of **14** to afford precursor **23** in 96% yield.

The *o*-diethynyl isomer **29** was obtained from bromopyridine **24**[22] using the same synthetic route as that for the preparation of **15** and **23** from **10** and **18**, respectively. Thus, the low-temperature lithiation of **24** followed by treatment with ICH_2CH_2I afforded **25** in 93% yield. The coupling reaction between **25** and TIPSA in Et_3N with $PdCl_2(PPh_3)_2$ and CuI catalysts proved to be surprisingly sluggish at ambient temperature. However, subsequent heating of the reaction at 75 °C for 3 d resulted in complete consumption of **25** and the isolation of **26** in 64% yield. Selective K_2CO_3-mediated desilylation of **26** gave **27** in 99% yield which was then coupled to afford **28** in 65% yield and the latter finally deprotected to provide **29** in 65% yield after workup. In a similar way to the deprotection of **11 to 16**, the $[(n\text{-}Bu)_4N]F$-mediated desilylation of **25** afforded ethynylpyridine **30**, which was obtained in 76% yield. With a modular palate of simple macrocycle precursors in hand, synthetic strategies toward the construction of dehydropyridoannulene architectures could then be explored.

Synthesis and Characterization of 1. In earlier work, cycles **7** and **8** were discovered to exhibit interesting luminescence and metal ion sensory properties. These materials comprise pyridines at the corners and bridging aromatic rings incorporated into the sides of the macrocyclic architecture.

With the eventual goal of generating 3-D coordination networks with novel physicochemical properties, it was obviously of high interest to evaluate the luminescence and metal coordination properties of the structurally related cycle **1**, a nitrogen heterocyclic analogue of dehydrotetrabenzo[20]annulene.[10d]

The synthesis of **1** was successfully accomplished using a route with two initially differing approaches to the common intermediate **33** (Scheme 2). In the first approach, iodopyridine **11** and diethynylpyridine **21** were coupled in Et_3N with $PdCl_2(PPh_3)_2$ and CuI catalysts to afford **31** in 75% yield. Dipyridine **31** was selectively desilylated with K_2CO_3 in MeOH to give **32** in 91% yield and the latter coupled in the presence of CuCl catalyst in oxygenated pyridine to provide **33** in 77% yield. In the second approach, **33** was obtained in 48% yield upon a Sonogashira reaction between **19** and **15**. The catalyst $[PdCl_2(dppf)]{\cdot}CH_2Cl_2$ was found to give superior quantities of product compared to $PdCl_2(PPh_3)_2$. The moderate yield of **33** in this case is partly attributable to the limited solubility and heat sensitivity of precursor **15**. When the latter reaction was conducted in Et_3N or THF at ambient temperature, the **15** failed to dissolve and slowly decomposed, subsequent heating also accelerated its decomposition. Hot toluene was found to be the most suitable solvent for the coupling reaction as it solubilized **15** with a minimal amount of degradation. The heat stable **33** was then deprotected with $[(n\text{-}Bu)_4N]F$ to afford **34** in 99%

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(14) The construction of ethynyl macrocycles incorporating pyridine and pyridine-type heterocycles has recently been the focus of a surge in interest. For examples incorporating pyridine units, see: (a) Baxter, P. N. W. *J. Org. Chem.* **2004**, *69*, 1813. (b) Yamaguchi, Y.; Kobayashi, S.; Miyamura, S.; Okamoto, Y.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 366. (c) Baxter, P. N. W. *Chem. Eur. J.* **2003**, *9*, 2531. (d) Campbell, K.; McDonald, R.; Ferguson, M. J.; Tykwinski, R. R. *Organometallics* **2003**, *22*, 1353. (e) Campbell, K.; McDonald, R.; Tykwinski, R. R. *J. Org. Chem.* **2002**, *67*, 1133. (f) Campbell, K.; McDonald, R.; Branda, N. R.; Tykwinski, R. R. *Org. Lett.* **2001**, *3*, 1045. (g) Sun, S.-S.; Lees, A. J. *Organometallics* **2001**, *20*, 2353. (h) Bosch, E.; Barnes, C. L. *Organometallics* **2000**, *19*, 5522. (i) Tobe, Y.; Nagano, A.; Kawabata, K.; Sonoda, M.; Naemura, K. *Org. Lett.* **2000**, *2*, 3265. (j) Tobe, Y.; Nakanishi, H.; Sonoda, M.; Wakabayashi, T.; Achiba, Y. *J. Chem. Soc., Chem. Commun.* **1999**, 1625. For examples of conjugated ethynyl macrocycles incorporating bipyridine units, see: (k) Venturi, M.; Marchioni, F.; Balzani, V.; Opris, D. M.; Henze, O.; Schlüter, A. D. *Eur. J. Org. Chem.* **2003**, 4227. (l) Baxter, P. N. W. *Chem. Eur. J.* **2002**, *8*, 5250. (m) Henze, O.; Lentz, D.; Schäfer, A.; Franke, P.; Schlüter, A. D. *Chem. Eur. J.* **2002**, *8*, 357. (n) Baxter, P. N. W. *J. Org. Chem.* **2001**, *66*, 4170. (o) Henze, O.; Lentz, D.; Schlüter, A. D. *Chem. Eur. J.* **2000**, *6*, 2362. (p) Henze, O.; Lehmann, U.; Schlüter, A. D. *Am. Chem. Soc. Polym. Mater. Sci. Eng.* **1999**, *80*, 231. For ethynyl macrocycles incorporating terpyridine units, see: (q) Grave, C.; Lentz, D.; Schäfer, A.; Samori, P.; Rabe, J. P.; Franke, P.; Schlüter, A. D. *J. Am. Chem. Soc.* **2003**, *125*, 6907. (r) Baxter, P. N. W. *Chem. Eur. J.* **2003**, *9*, 5011.

(15) The term “true dehydroarylannulene” is used in this context to exclude arene cyclynes in which one or more of the bridging aryl groups exhibit meta-, para-, and other types of non-*ortho*-connectivity.

(16) . Although the pyridine nitrogens can be arranged in 64 possible ways within **3**, the macrocycle is actually one of only 12 different regioisomers due to symmetry overlaps. For the same reason, **2** is one of 10 different regioisomers generated from 16 possible pyridine nitrogen arrangements. However in **1**, there are 256 possible pyridine nitrogen arrangements giving rise to 76 different regioisomers!

(17) Reports on the syntheses of *o*-diethynylpyridines are rare. See: (a) ref 14c. (b) Kim, C.-S.; Russell, K. C. *J. Org. Chem.* **1998**, *63*, 8229. (c) Gibson, K. J.; d’Alarcao, M.; Leonard, N. J. *J. Org. Chem.* **1985**, *50*, 2462.

(18) (a) Talik, T.; Talik, Z. *Roczniki Chem.* **1962**, *36*, 539. (b) Talik, T. *Roczniki Chem.* **1962**, *36*, 1049. (c) Imahori, T.; Uchiyama, M.; Sakamoto, T.; Kondo, Y. *Chem. Commun.* **2001**, 2450.

(19) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(20) Bell, M. L.; Chiechi, R. C.; Johnson, C. A.; Kimball, D. B.; Matzger, A. J.; Wan, W. B.; Weakley, T. J. R.; Haley, M. M. *Tetrahedron* **2001**, *57*, 3507.

(21) (a) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320. (b) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275. For an example of the application of the Hay procedure to the synthesis of polypyridylbutadiynes, see: (c) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491.

yield.[23] Diethyne **34** was found to be somewhat more stable to heat and light than its precursor **15**, although its ambient temperature solubility in a range of organic solvents remained comparable.

Final intramolecular cyclization of **34** into **1** was achieved using the Eglinton–Galbraith protocol that had been found to be most successful for the preparation of **7** and **8**.[24] Thus, **34** was cyclized under medium/high dilution conditions in degassed pyridine with an excess of $[Cu_2(OAc)_4]\cdot 2H_2O$ to afford **1** in 40% isolated yield. Cycle **1** was found to be stable in refluxing toluene at 110 °C, but underwent color darkening upon exposure to daylight over days to weeks.

The proposed structure of the product isolated from the coupling of **34** was established to be that of **1** (Scheme 2) on the basis of mass spectroscopic, infrared, and ^1H and ^{13}C NMR spectroscopic studies including $^1H-^1H$ COSY and $^1H-^{13}C$ HSQC/HMQC measurements.

The FAB mass spectrum of the coupling product displayed a single isotope cluster peak at $m/z = 453$, matching that calculated for the $[M^+ + H]$ isotopic envelope of macrocycle **1**. This structural assignment was further substantiated by a high-resolution FAB mass spectroscopic measurement of the $[M^+ + H]$ isotopic envelope, which confirmed the exact elemental composition of the product to be $C_{32}H_{13}N_4$, in accordance with the macrocyclic structure **1** plus one hydrogen.

In the infrared spectrum of **1**, vibrational modes characteristic of the H−C≡ stretch of terminal alkynes were absent, establishing that the coupling product is a macrocycle, and not a linear oligomer with unreacted terminal ethyne groups.

The ^{13}C NMR spectrum comprised eight peaks, consistent with the above macrocyclic structural assignment for **1** (Figure 1). The chemical shifts of the three peaks in the range 91.5–80.1 ppm correspond to the chemically and magnetically inequivalent carbons of the butadiynes and the equivalent carbons of the bridging alkyne groups. The remaining five peaks originate from the carbons of the pyridines.

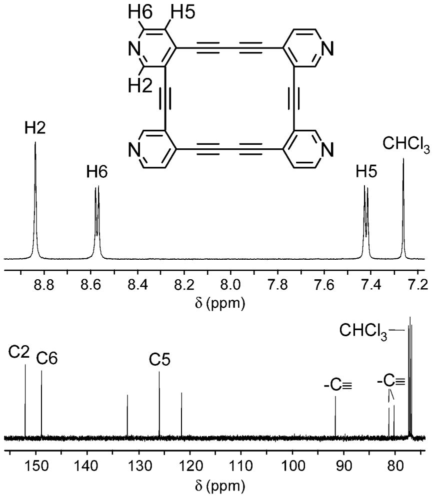

FIGURE 1. 400 MHz ^1H (upper) and 100.6 MHz ^{13}C (lower) NMR spectra of **1**, recorded in $CDCl_3$ solution at 25 °C.

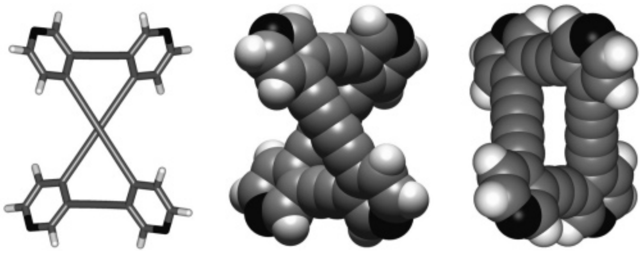

FIGURE 2. Energy-minimized structure of macrocycle **1**. Left: plan view (stick representation). Center: plan view (CPK representation). Right: view through central macrocyclic cavity. The minimization was obtained by an AM1 semiempirical calculation using SPARTAN 02 Linux/Unix, Wavefunction, Inc., Irvine, CA.

The ^1H NMR spectrum displayed three resonances expected for the macrocyclic structure **1** (Figure 1). A $^1H-^1H$ COSY measurement verified that it was a single compound and not a mixture of species. Peaks originating from the protons of terminal ethynes were absent in the ^1H NMR spectrum, lending further support for the macrocyclic identity of this compound. Spectral assignments were made on the basis of coupling constants and spectral comparisons with the precursors.

A semiempirical AM1 molecular modeling calculation performed upon the structure assigned to **1** showed the ground-state conformation to be that of a strain-free twisted, chiral macrocycle, with a small internal void (Figure 2).[25]

Synthesis and Characterization of 2. A further avenue of interest would be to generate dehydroannulene coordination polymers of lower dimensionality than those expected for **1**. Polymers of this type may function as conjugated wires and new luminescent materials, but with additional structural features such as enhanced conjugation and chirality.[26a–g] Toward this goal, the exotopic bidentate macrocycle **2** was synthesized, which is a structural hybrid between **1** and dehydrotetrabenzo-[20]annulene, the benzo-analogue of **1**.

A viable route to **2** was developed utilizing diethynylpyridine **21** (Scheme 3). Thus, **36** was isolated from

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[22] Sakamoto, T.; Nagata, H.; Kondo, Y.; Sato, K.; Yamanaka, H. *Chem. Pharm. Bull.* **1984**, *32*, 4866.

[23] Unambiguous assignments of the NMR proton resonances of **31**–**33** to their respective pyridine rings were achieved using COSY, NOESY and ROESY measurements. First, the COSY spectral connectivities revealed the groups of protons that originated from the same pyridine rings. Second, the NOESY and ROESY spectra displayed characteristic "through-space" interactions identifying the particular substituted ring to which each group of pyridine protons belonged. For example, molecular modeling indicated that the TIPSA substituent in **31**–**33** contributed to hindered rotation of all the pyridines, and suggestive of a strong "through-space" interaction between the TIPS and the 2H protons of the pyridines without the TIPSA groups. In each case, a strong NOESY cross-peak was indeed observed between the signals due to the TIPS group and one of the pair of peaks corresponding to the pyridine 2H protons. The pyridine 2H contributing to the cross-peak with the TIPS group was therefore assignable to the ring which did not bear the TIPSA substituent. The NOESY spectra of **31**–**33** displayed additional evidence supportive of the latter assignments, which in each case comprised a weaker cross-peak between the TIPS signal and that of the adjacent 5H proton connected to the same pyridine ring. In **32**, an NOESY cross-peak was also observable between the TIPS signal and that of the terminal alkyne proton. The protons of **34** were assigned on the basis of NMR spectral comparisons with **32** and **33**.

[24] Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 72–75.

[25] For an example of the use of semiempirical AM1 calculations for successfully predicting the conformations of ethynyl macrocycles, see: Srinivasan, M.; Sankararaman, S.; Hopf, H.; Dix, I.; Jones, P. G. *J. Org. Chem.* **2001**, *66*, 4299.

the Sonogashira reaction between **21** and **35**[14n] in 77% yield and then selectively desilylated with K_2CO_3 in MeOH to afford **37** in 88% yield after workup. Diethynylpyridine **37** was subsequently self-coupled with CuCl catalyst in oxygenated pyridine to give **38** in 94% yield and the latter deprotected with $[(n\text{-Bu})_4N]F$ to afford **39** in 91% yield after purification. The intramolecular cyclization of **39** was again most effectively accomplished using excess $Cu_2(OAc)_4$ under medium/high dilution conditions in degassed pyridine to provide **2** in a particularly good yield of 79%.[27] Cycle **2** was similar to **1** with respect to its stability toward heat and light.

In parallel to the above synthesis, an alternative route to **2** was also investigated using **15** and **41**. Iodophenyl **41** was prepared from **40**[28] via the halogen-exchange protocol previously used for the synthesis of **11**, **19**, and **25**. Thus, the palladium-catalyzed coupling between **15** and **41** using identical conditions to that of the generation of **33** from **15** and **19** afforded **42** in 48% yield. However, this route to **2** was abandoned in favor of the former, as it offered no further advantage in terms of improved overall yield.

The macrocyclic structural formulation of **2** (Scheme 3) was established using the same spectroscopic techniques as in **1**. The FAB mass spectrum exhibited a single isotope cluster peak at *m/z* = 451, corresponding to the calculated $[M^+ + H]$ isotopic envelope of macrocycle **2**. The high-resolution FAB mass spectroscopic measurement of the $[M^+ + H]$ isotopic envelope confirmed the exact elemental composition of the product to be $C_{34}H_{15}N_2$.

The ^{13}C NMR spectrum exhibited the expected seventeen peaks, i.e., six peaks from 94.9 to 78.0 ppm corresponding to the carbons of the bridging alkyne groups, and the remaining eleven originating from the carbons of the aryl rings (Figure 3). The phenyl C3/6 and C4/5 carbons as well as the pyridine C5 carbon were additionally assigned on the basis of ^{13}C DEPT measurements. Vibrational modes and peaks characteristic of the H−C≡ group were absent in the infrared and ^1H NMR (Figure 3) spectra, again supportive of a macrocyclic rather than linear oligomeric or polymeric material. $^1H-^1H$ COSY measurements also verified that it was a single compound and not a mixture of species.

Synthesis and Characterization of 3. Since the first reported independent syntheses of dehydrotribenzo[12]-annulene by Staab and Eglinton and their respective coworkers,[29a−b] triangular dehydrotriaryl[*n*]annulenes (*n* = 12, 18) have attracted a considerable amount of interest.[6a−d] For example, they have been used as precursors for the attempted construction of sections of the hypothetical carbon polymer networks graphyne and graphdiyne and have also been demonstrated to exhibit a rich coordination chemistry involving metal complexation to the triple bonds.[6c] Surprisingly, very few studies have been reported on the synthesis and properties of heterocyclic analogues of dehydrotriaryl[*n*]annulenes other than those incorporating thiophene rings.[30a−j] We therefore describe below some of our hitherto unpub-

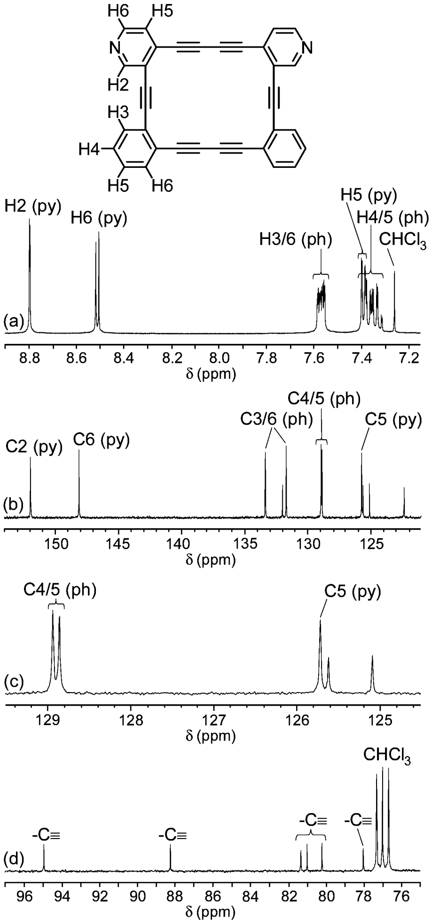

FIGURE 3. 400 MHz ^1H (a) and 100.6 MHz ^{13}C NMR spectra of **2** (showing (b) aromatic region, (c) expansion of phenyl C4/5 and pyridyl C5 resonances, (d) alkyne region), recorded in $CDCl_3$ solution at 25 °C.

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[26] For the generation of 1-D coordination polymers using ethynylpyridine-type ligands, see: (a) Kim, H.-J.; Zin, W.-C.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 7009. (b) Zaman, Md. B.; Smith, M. D.; zur Loye, H.-C. *Chem. Commun.* **2001**, 2256. (c) Fiscus, J. E.; Shotwell, S.; Layland, R. C.; Smith, M. D.; zur Loye, H.-C.; Bunz, U. H. F. *Chem. Commun.* **2001**, 2674. (d) Jouaiti, A.; Jullien, V.; Hosseini, M. Wais.; Planeix, J.-M.; De Cian, A. *Chem. Commun.* **2001**, 1114. (e) Ciurtin, D. M.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. *Chem. Mater.* **2001**, *13*, 2743. (f) ref 13d. (g) Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 2027.

[27] The yield disparity between **1** (40%) and **2** (79%) is somewhat surprising considering the similarity in reaction conditions and workup. It may be noted however, that the cyclization of **34** to **1** was effected using $[Cu_2(OAc)_4]\cdot 2H_2O$, whereas anhydrous $Cu_2(OAc)_4$ was used for the cyclisation of **39** to **2**. The presence of coordinated water may exert a detrimental effect upon the cyclization reaction in specific cases, but further experimental investigations will be necessary in order to verify this hypothesis.

[28] Collins, S. K.; Yap, G. P. A.; Fallis, A. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 385.

[29] (a) Staab, H. A.; Graf, F. *Tetrahedron Lett.* **1966**, 751. (b) Campbell, I. D.; Eglinton, G.; Henderson, W.; Raphael, R. A. *Chem. Commun.* **1966**, 87.

[30] For dehydroannulenes incorporating nitrogen heterocycles, see: (a) Ott, S.; Faust, R. *Synlett.* **2004**, 1509. (b) García-Frutos, E. M.; Fernández-Lázaro, F.; Maya, E. M.; Vázquez, P.; Torres, T. *J. Org. Chem.* **2000**, *65*, 6841. (c) van Roosmalen, J. H.; Jones, E.; Kevelam, H. *Tetrahedron Lett.* **1972**, *13*, 1865. It may be noted however that in the former two references, the alkynes are not directly connected to the heterocyclic rings but are actually connected to benzenes which are fused to the heterocycles. For reports on the syntheses of dehydroannulenes incorporating thiophenes, see: (d) Boydston, A. J.; Haley, M. M.; Williams, R. V.; Armantrout, J. R. *J. Org. Chem.* **2002**, *67*, 8812. (e) Marsella, M. J.; Piao, G.; Tham, F. S. *Synthesis* **2002**, 1133. (f) Marsella, M. J.; Wang, Z.-Q.; Reid, R. J.; Yoon, K. *Org. Lett.* **2001**, *3*, 885. (g) Sarkar, A.; Haley, M. M. *Chem. Commun.* **2000**, 1733. (h) Zhang, D.; Tessier, C. A.; Youngs, W. J. *Chem. Mater.* **1999**, *11*, 3050. (i) Iyoda, M.; Vorasingha, A.; Kuwatani, Y.; Yoshida, M. *Tetrahedron Lett.* **1998**, *39*, 4701. (j) Solooki, D.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1994**, *13*, 451.

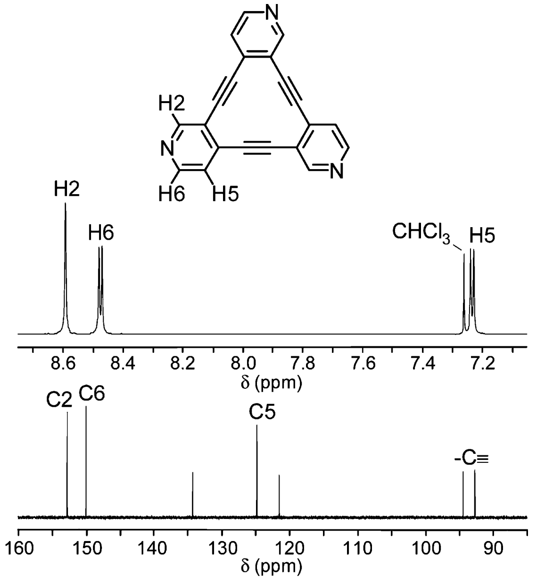

FIGURE 4. 500 MHz ^{1}H (upper) and 125.8 MHz ^{13}C (lower) NMR spectra of **3**, recorded in $CDCl_3$ solution at 25 °C; [**3**] = 3.3×10^{-2} M.

lished results on the synthesis and spectroscopic properties of **3**, a dehydrotripyrido[12]annulene.

The synthesis of **3** was accomplished in two steps from **16** as shown in Scheme 4. Thus, treatment of an argon-purged aqueous ammoniacal solution of $CuSO_4{\cdot}5H_2O$ with $NH_2OH{\cdot}HCl$, followed by addition of **16**, resulted in the formation of the highly insoluble cuprate **43**, which was isolated in 95% yield. Cyclotrimerization of **43** using the classical Stephens−Castro protocol afforded **3** as the sole cyclic product in 5% yield after purification. Cycle **3** exhibited greater stability toward heat and light compared to **1** and **2**.

The low yield of **3** is in sharp contrast to that of the reported 48% for the related Stephens−Castro cyclization to give dehydrotribenzo[12]annulene.[31a] An explanation may lie in the possibility that cuprate **43** exists as a linear or cross-linked coordination polymer in the solid state, held together by Cu−N and Cu−alkyne coordination interactions. In such a situation, polymer formation would negate against cyclization by clamping the iodine and copper reaction sites into fixed arrangements, at distances and angles unfavorable for intramolecular ring closure. The heterogeneous nature of the cyclization reaction lends further support to the possibility that **43** is an insoluble coordination polymer.

The macrocyclic structural formulation of **3** (Scheme 4) was established as for **1** and **2**, on the basis of multiple spectroscopic studies. The ^{1}H and ^{13}C NMR spectra comprised the expected three and seven peaks, respectively (Figure 4). In the case of the ^{1}H NMR and infrared spectra, peaks characteristic of the H−C≡ group were absent. The infrared spectrum of the cyclization product displayed two bands at 2227 and 2212 cm^{-1} due to the presence of a C≡C bond, indicating that isomerization to a tris(pyridocyclobutadieno)benzene system had not occurred.[32a,b] The FAB mass spectrum exhibited a single cluster peak at $m/z = 304$ corresponding to the [$M^+ + H$] ion of **3**, and the high-resolution FAB mass spectrum of the [$M^+ + H$] isotopic envelope confirmed the elemental composition of the product to be $C_{21}H_{10}N_3$. A semiempirical AM1 calculation confirmed **3** to possess a rigid, strain-free planar geometry with a small internal void (Figure 5).

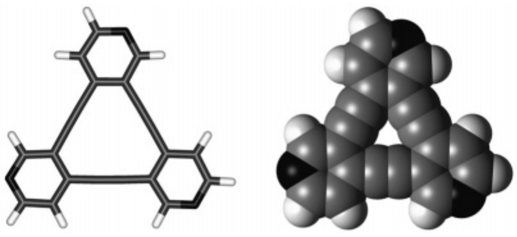

FIGURE 5. Energy-minimized structure of macrocycle **3** (plan view). Left: stick representation. Right: CPK representation. The minimization was obtained by an AM1 semiempirical calculation using SPARTAN 02 Linux/Unix, Wavefunction, Inc., Irvine, CA.

Interestingly, the ^{1}H NMR spectrum of **3** in $CDCl_3$ was concentration dependent. For example, reducing the [**3**] from 3.3×10^{-2} M (a saturated solution at 25 °C) to 1.3×10^{-3} M resulted in a downfield shift of all protons H2, H6, and H5 by $\Delta\delta$ = 0.023, 0.020, and 0.024 ppm, respectively. The latter behavior was reversible and is indicative of an aggregation/deaggregation process, mediated by $\pi-\pi$ interactions, which would be expected of a rigid, planar molecule such as **3**. Thus, the net deshielding of the protons of **3** upon dilution is consistent with the breaking up of aggregates.

Spectroscopic Properties of 1, 2, and Precursors 33, 34, 38, 39, and 42. Solutions of **1** and **2** in CH_2Cl_2 displayed similar UV−vis spectra which exhibited two high energy absorptions at 255−269 nm with relatively large extinction coefficients where $\epsilon = (1.20-1.29) \times 10^5$ M^{-1} cm^{-1}. In both cycles, a series of three to four poorly resolved absorption envelopes were also observable at lower energies between 294 and 354 nm with considerably reduced extinction coefficients where $\epsilon = (0.10-0.35) \times 10^5$ M^{-1} cm^{-1} (Figures 6 and 7). All absorptions were invariant in energy and shape below 3.9×10^{-5} M, showing that **1** and **2** were not aggregating in dilute solution.

The UV−vis spectra of the precursors **33**, **34**, **38**, **39,** and **42** were also similar to each other, comprising one to two relatively high energy absorptions within the range 237−253 nm and a series of three to four lower energy absorptions between 284 and 375 nm, which were particularly well resolved in **39** (Figures 6 and 7). In **33** and **34**, all absorptions were invariant in energy and shape below 8.8×10^{-5} M, showing that these precursors were not aggregating in dilute solution. However, the intense bands from 237 to 253 nm in the spectra of **38**, **39**, and **42**, broadened and shifted 2−3 nm to lower energy at concentrations higher than 5×10^{-5} M. The precursors incorporating both phenyl and pyridyl rings

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[31] (a) Solooki, D.; Ferrara, J. D.; Malaba, D.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J.; John, J. A.; Tour, J. M. *Inorg. Synth.* **1997**, *31*, 122. For an alternative preparation of dehydrotribenzo[12]-annulene by cyclotrimerisation of 2-bromophenylacetylene under phase transfer conditions using [$Pd(PPh_3)_4$]/CuI catalysts, see: (b) Huynh, C.; Linstrumelle, G. *Tetrahedron* **1988**, *44*, 6337.

[32] (a) Nambu, M.; Mohler, D. L.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 6138. (b) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.

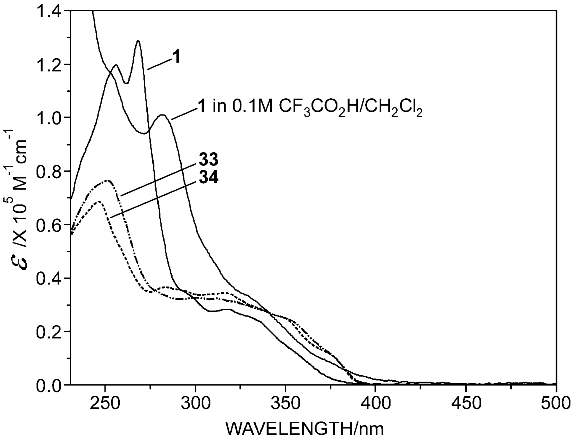

FIGURE 6. UV−vis absorption spectra of **1** and precursors **33** and **34** recorded in CH_2Cl_2 solution and also **1** in CH_2Cl_2 (0.1 M in CF_3CO_2H) at 25 °C.

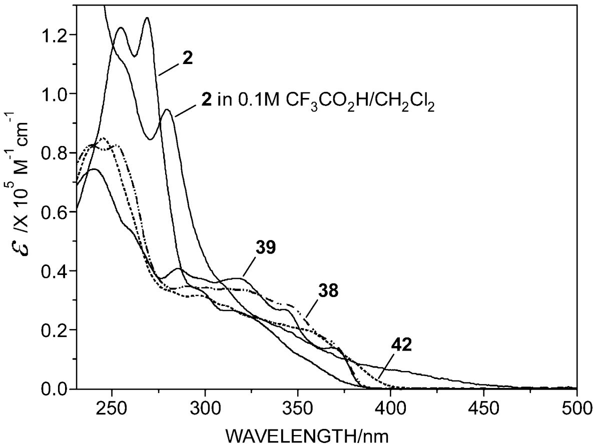

FIGURE 7. UV−vis absorption spectra of **2** and precursors **38**, **39**, and **42** recorded in CH_2Cl_2 solution and also **2** in CH_2Cl_2 (0.1 M in CF_3CO_2H) at 25 °C.

may thus be undergoing some degree of ground-state aggregation at, and above, the latter concentration threshold.

Although the overall shape of the UV−vis spectra of all compounds studied were approximately similar, differences in detail were evident upon comparison of the spectra of the macrocycles with the precursors. For example, the 255−269 nm absorptions in **1** and **2** are shifted to slightly lower energy compared to the related absorptions of the precursors at 237−253 nm. The extinction coefficients of the 255−269 nm absorptions in **1** and **2** are also significantly higher than those of the 237−253 nm precursor absorptions, which lie within the range (0.69−0.85) × 10^5 $M^{-1}cm^{-1}$.

However, the overall absorptions of **38**, **39**, and **42** from 280 to 370 nm occur at relatively higher extinction coefficients compared to that of **2** within the same wavelength range. In addition, the lower energy absorption complex of **42** extends to 400 nm. A similar trend is found for **33** and **34**, where the overall absorption curves from 280 to 380 nm occur at higher extinction coefficients and tail to a lower energy compared to that of **1** within the same wavelength range. Finally, the UV−vis absorption spectra of CH_2Cl_2 solutions of **1** and **2** were found to be sensitive to the presence of strong organic acids such as CF_3CO_2H (Figures 6 and 7). Treatment of the acidified solutions of **1** and **2** with aqueous Na_2CO_3 resulted in regeneration of the original free ligand spectra, verifying that reversible protonation was occurring rather than irreversible chemical reactions.

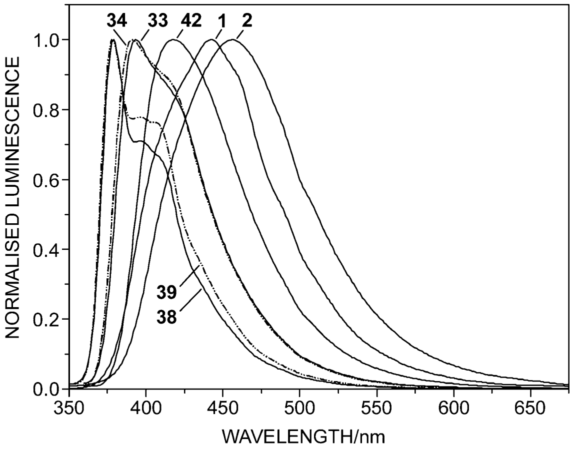

FIGURE 8. Normalized fluorescence emission spectra of **1**, **2**, **33**, **34**, **38**, **39**, and **42** recorded in CH_2Cl_2 solution at 25 °C. (See the Experimental Section for the respective excitation energies and solution concentrations.)

Solutions of **1**, **2**, **33**, **34**, **38**, **39,** and **42** in organic solvents were fluorescent when exposed to UV light. The emissions of **1** and **2** in aerated and deoxygenated CH_2Cl_2 solution each comprised a single broad maximum at 443 and 456 nm, respectively, when excited within their lower energy absorption envelopes (Figure 8). The excited states of **1** and **2** were therefore insensitive to quenching by oxygen. The energy of the emission maxima also remained unchanged below 8.8−9.8 × 10^{-5} M, showing that excited-state aggregation of the cycles was not occurring in dilute solution.

The fluorescence spectra of precursors **33** and **34** were virtually identical, comprising a relatively sharp emission at 391−393 nm and a broader shoulder at 414 nm. The fluorescence spectra of **38** and **39** were also very similar, exhibiting a sharp emission at 378−379 nm and two shoulders at 397 and 407−409 nm, respectively (Figure 8). The TIPS substituents therefore exercise a negligible effect upon the excited-state energies of the precursors. The emission of **1** on the other hand, is 51 nm lower in energy than that of the averaged highest energy emissions of **33** and **34**. The emission of **2** is 77 nm lower in energy than that of the highest energy emissions of its precursors **38** and **39**. Cyclization therefore causes a significant lowering of the excited-state energies compared to that of the precursors. Interestingly, the fluorescence spectrum of **42** was unlike those of **33**, **34**, **38**, and **39**, comprising a single broad emission at 417 nm, and of intermediate energy between the latter precursors and the cycles **1** and **2** (Figure 8). The inclusion of both phenyl and pyridyl aromatic units within the macrocyclic structures therefore result in a lowering of the excited-state energies. The differences in emission energies between the **33/34** pair and **42** also suggests that variation of the relative arrangements of phenyl versus pyridyl rings within these systems may be used to controllably tune their fluorescence energies.

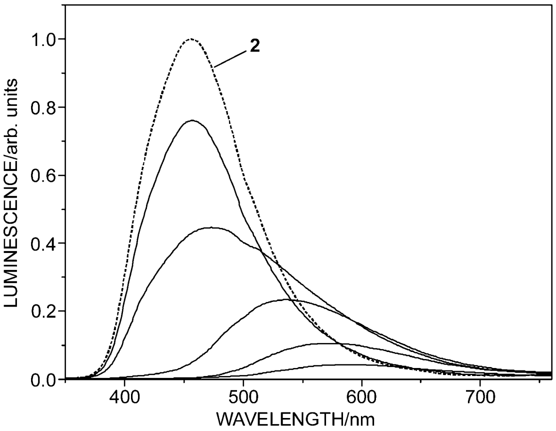

FIGURE 9. Luminescence emission spectra of **2** with incremental additions of CF_3CO_2H at [**2**] = 9.8×10^{-5} M in CH_2Cl_2 and [H^+] of, respectively, 1×10^{-4}, 1×10^{-3}, 1×10^{-2}, 1×10^{-1}, and 1.0 M. The spectra were recorded 48 h after solution preparation (λ_{ex} = 318 nm).

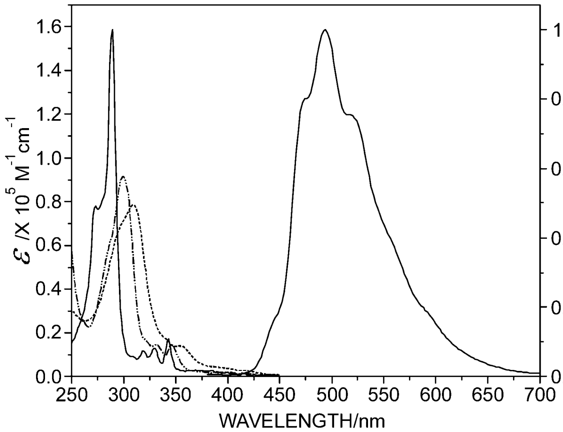

FIGURE 10. UV−vis spectra (left) of **3** in CH_2Cl_2 (—), **3** in CH_2Cl_2/0.1 M CF_3COOH (− • •), 1:3 **3**/$PdCl_2(MeCN)_2$ in 10% MeOH/CH_2Cl_2 (• • •), and fluorescence emission spectrum (right, —) in CH_2Cl_2.

It may also be noted that the fluorescence emissions of **33**, **34**, **38**, **39,** and **42** in aerated and deoxygenated CH_2Cl_2 solution also remained identical in shape and energy, showing that their excited states were insensitive to quenching by oxygen. Interestingly, the highest energy emissions of **33**, **34**, **38**, and **39** exhibited 2−3 nm shifts to lower energy at concentrations $\geq 7 \times 10^{-5}$ M, suggesting that excited-state aggregation phenomena were beginning to occur within this concentration domain.

The luminescence emissions of **1** and **2** were also sensitive to the presence of organic acids. For example, incremental additions of CF_3CO_2H to both **1** and **2** resulted in a stepwise quenching of their respective emissions and with a concomitant shift in the emission maxima to lower energies (shown for **2** in Figure 9). The spectra gradually decreased in intensity and energy over several days, suggesting that kinetically controlled excited-state aggregation processes were operative. The effect of the weaker acids CH_3CO_2H and $PhCO_2H$ on the luminescence of **2** were also investigated. The luminescence of 9.8×10^{-5} M solutions of **2** in 1:1 CH_3CO_2H/CH_2Cl_2 and in 0.1 M $PhCO_2H/CH_2Cl_2$ was partially quenched and shifted to lower energy by 74 and 8 nm at 530 and 464 nm, respectively, upon excitation at 318 nm. Interestingly, the fluorescence of 9.8×10^{-5} M solutions of **2** were completely quenched in the presence of aromatic nitro compounds such as nitrobenzene at a concentration of 0.1 M and 2,4,7-trinitrofluoren-9-one (TNF) at a ratio of 10:1 TNF/**2**. The latter result suggests the possibility that **2** may be able to participate in $\pi-\pi$ interactions with nitro-aromatics.

Spectroscopic Properties and Luminescence Cation Sensing by 3. The UV−vis spectrum of **3** in CH_2Cl_2 was rather unusual, exhibiting seven absorbances including a particularly intense and sharp band at 288 nm which were invariant in energy and shape below [**3**] = 2.7×10^{-5} M, showing that aggregation is not occurring in dilute solution (Figure 10). Cycle **3** is also a fluorescent chromophore, CH_2Cl_2 solutions affording a green emission upon exposure to UV light. The fluorescence emission spectrum of **3** comprised three bands at 474, 494, and 524 nm, which did not change in shape and energy below 3.3×10^{-5} M, showing that excited-state aggregation was absent in dilute solution. The fluorescence spectra of aerated and argon-bubbled solutions of **3** were also identical, eliminating the possibility of oxygen-mediated excited-state quenching. Interestingly, **3** exhibited a rather large Stokes shift of 206 nm between the highest intensity absorption and emission bands (Figure 10).

As stated above, cycles **4**−**8** are strongly fluorescent chromophores which were discovered to function as highly effective luminescence sensors for particular metal ions. Of the macrocycles **1**−**3** reported herein, cycle **3** exhibits the greatest structural differences compared to **4**−**8**. It was therefore anticipated that **3** would also exhibit significantly different luminescence sensory properties toward metal ions.[33]

A detailed UV−vis spectroscopic investigation into the ion-binding properties of **3** with 1:3 stoichiometric mixtures of **3**/M^{n+} in 10% MeOH/CH_2Cl_2, where [**3**] = 5.4×10^{-6} M and M^{n+} = Li^I, Na^I, K^I, Mg^{II}, Ca^{II}, Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Pt^{II}, Au^I, Ag^I, Cu^I, Cu^{II}, Zn^{II}, Cd^{II}, Hg^{II}, Pb^{II}, Tl^I, Al^{III}, In^{III}, Sc^{III}, Y^{III}, La^{III}, Eu^{III}, and Tb^{III}, showed zero or minimal changes compared to the spectrum of pure **3**, indicating insignificant binding of the macrocycle to the above cations in dilute solution.[34] However, the UV−vis spectra of 1:3 **3**/Pd^{II} in 10% MeOH/CH_2Cl_2 and **3**/CF_3CO_2H in CH_2Cl_2, where [**3**] = 5.4×10^{-6} M and [H^+] = 0.1 M, were significantly different from the spectrum of pure **3**, demonstrating that Pd^{II} coordination and protonation was occurring (Figure 10). The fluorescence emis-

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(33) For a recent overview on fluorescent molecular sensors for cation recognition, see: Valeur, B.; Leray, I. *Coord. Chem. Revs.* **2000**, *205*, 3.

(34) The metal chlorides and complexes used in the study were $CrCl_3\cdot 6H_2O$, $FeCl_2$, $CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$, $PdCl_2(MeCN)_2$, $PtCl_2(MeCN)_2$, $[Cu(MeCN)_4]BF_4$, and AuCl(THT). All remaining cations investigated were in the form of their anhydrous triflates. With the exception of $PdCl_2(MeCN)_2$, $[Cu(MeCN)_4]BF_4$, and AuCl(THT), all stock solutions were prepared in MeOH. The chromium, iron, cobalt and nickel chlorides were each dissolved in a drop of distilled water prior to the preparation of the standard solutions in methanol to ensure complete solubility. For the same reason, the palladium and platinum complexes were initially dissolved in 1 mL of warm acetonitrile, and in the former case diluted to the required volume with CH_2Cl_2. The AuCl(THT) solution was prepared in CH_2Cl_2 and the $[Cu(MeCN)_4]BF_4$ solution in MeCN. The $Hg(CF_3SO_3)_2$ was prepared from the reaction between HgO and $(CF_3SO_2)_2O$.[14c] The Cu^{II}, Ag^I, and Tl^I triflates used were ≥ 99.9% purity.

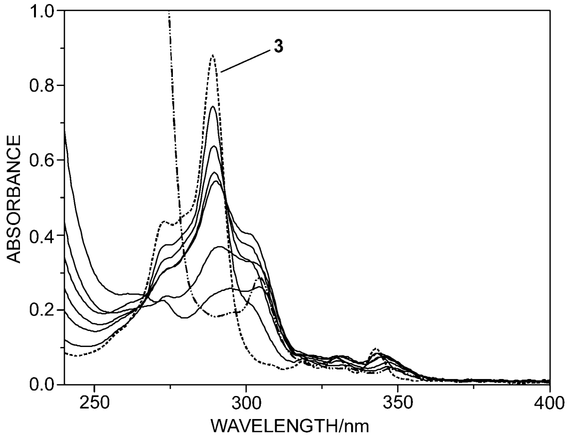

FIGURE 11. UV−vis spectra of 5.4×10^{-6} M solutions of **3** in 10% $MeOH/CH_2Cl_2$ titrated with incremental additions of $Hg(CF_3SO_3)_2$, where the **3**/Hg^{II} ratios are respectively 1:5, 1:10, 1:15, 1:20, 1:30, 1:50 (—), and 1:500 (− • •). The spectra were recorded 40 h after solution preparation at 25 °C.

sion spectra of the above **3**/CF_3CO_2H and all of the 1:3 **3**/M^{n+} solutions were then recorded. Of all cations studied, only Pd^{II} and protonation[35] caused quenching of the free ligand fluorescence. All other metals investigated afforded zero changes in the emissions of the macrocycle. The detection limit for Pd^{II} was estimated to be $[Pd^{II}] = 1 \times 10^{-6}$ M. The above results therefore demonstrate that **3** functions as a highly selective fluorescence quenching sensor for Pd^{II}.

The fact that **3** possesses exotopic nitrogens suggests that it would exhibit similar metal ion binding behavior to the structurally related cycles **7** and **8** which coordinate Co^{II}, Ni^{II}, Ag^{I}, and Hg^{II} as well Pd^{II} in dilute solution. However, no evidence for the complexation of **3** to $M^{n+} = Co^{II}$, Ni^{II}, Ag^{I}, and Hg^{II} was observed for 1:3 ratios of **3**/M^{n+} where $[\mathbf{3}] = 5.4 \times 10^{-6}$ M. Interestingly, **3** was found to bind Hg^{II} when the metal salt was slightly more concentrated, i.e., at **3**/Hg^{II} ratios ≥1:5 with $[\mathbf{3}] = 5.4 \times 10^{-6}$ M in 10% $MeOH/CH_2Cl_2$ (Figure 11). The Hg^{II} binding also caused a quenching of the free ligand fluorescence. Cycles **7** and **8** signal the presence of Co^{II}, Ni^{II}, and Ag^{I} in dilute solution by forming insoluble coordination polymer precipitates. The reason **3** fails to bind to Co^{II}, Ni^{II}, Ag^{I} under dilute conditions may originate from the fact that it has less coordination sites compared to **7** and **8** and may thus be unable to form coordination polymers with sufficient cross-linking for precipitation. In contrast, ligands **4**−**6** display rather different metal ion-binding preferences dictated by their respectively endo- and exotopic bidentate coordination sites.[36] The metal ion complexation behavior of **3** and **4**−**8** are summarized and compared in Table 1 above.

TABLE 1. Coordination Preferences of Cycles L toward Metal Ions in Dilute Solution Determined by UV−vis Spectrophotometry

L	[L],[a] mol L^{-1}	L/M^{n+}	L/M^{n+} coordination preferences
3	$5.4 \times 10^{-6\,a}$	1:3	Pd^{II}
4	$6.6 \times 10^{-6\,b}$	1:1	$Co^{II} \cong Ni^{II} > Cu^{II} \cong Zn^{II}$
5	$1.1 \times 10^{-5\,b}$	1:1	$Cu^{II} \cong Ag^{I}$
6	$7.3 \times 10^{-6\,b}$	1:1.5	$Cu^{II} \cong Ag^{I} > Pd^{II} > Tl^{I} > Hg^{II}$
7	$8.6 \times 10^{-6\,a}$	1:4	$Pd^{II} > Co^{II} \cong Ni^{II} \cong Ag^{I} > Fe^{II} \cong Hg^{II}$
8	$9.6 \times 10^{-6\,c}$	1:4	$Pd^{II} \gg Ni^{II} > Co^{II} > Ag^{I} > Hg^{II}$

[a] The spectrophotometric measurements were performed in the following solvent mixtures: (a) 10% $MeOH/CH_2Cl_2$; (b) 33% $CHCl_3/MeOH$; (c) 10% $MeOH/CHCl_3$. See refs 14a,c,l,n.

The spectroscopic metal ion binding studies were conducted in dilute solutions where metal coordination interactions may be expected to be very weak. On the other hand, **3** would be expected to exhibit a richer complexation chemistry under more concentrated conditions. In order therefore to obtain an initial assessment of the potential of **3** to form coordination polymers, a 1:4 mixture of **3**/$AgBF_4$ was prepared by adding a solution of **3** in CH_2Cl_2 (1 mL; $[\mathbf{3}] = 4.4 \times 10^{-3}$ M) to a solution $AgBF_4$ in MeCN (1 mL). Precipitation of a pale yellow solid immediately ensued upon admixture of the reactants and was completed by gentle heating. The isolated solid was insoluble in all the usual laboratory solvents, a property characteristic of cross-linked coordination polymers, which severely hampered its characterization. However, treatment of the solid with hot aqueous KCN resulted in regeneration of the free ligand providing further evidence that coordination of Ag^+ to **3** had occurred.[37]

Thermal Behavior of Macrocycles and Precursors. Some dehydrobenzoannulenes and related carbon-rich structures have been reported to function as high

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[35] A 1:3 **3**/Pd^{II} ratio ($[Pd^{II}] = 1.62 \times 10^{-5}$ M) was sufficient to quench the luminescence of **3**, whereas a much greater proton concentration ($[CF_3COOH] = 0.1$ M) was required to quench the luminescence of **3** (where $[\mathbf{3}] = 5.4 \times 10^{-6}$ M) suggesting that the Pd^{II} is binding more strongly to **3** than protons. It may also be noted that all spectra of **1**−**3** in the presence of CF_3COOH were recorded in pure CH_2Cl_2. In 10% $MeOH/CH_2Cl_2$, the spectroscopic effects of protonation by CF_3COOH are further reduced due to preferential solvation of the acid by MeOH. Proton-controllable fluorescence phenomena have been reported for oligomeric linear, branched, and cyclic conjugated organic scaffolds incorporating nitrogen-donor heterocycles; see: (a) refs [14a,c,k,l]; (b) Martin, R. E.; Wytko, J. A.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1999**, *82*, 1470. (c) Pabst, G. R.; Pfüller, O. C.; Sauer, J. *Tetrahedron* **1999**, *55*, 5047. (d) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930.

[36] Cycles **4**−**6** incorporate bidentate complexation sites that would be expected to prefer metal ions with for example octahedral coordination geometries. This situation is found for **4**, which shows strong binding affinities for the ions Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} in dilute solution. However, **5** and **6** deviate from this expected behavior due to the presence of the hindering alkyne substituents in the 6,6′-positions of the 2,2′-bypyridines. Cycle **5** binds only Cu^{II} and Ag^{I}, presumably because it is a relatively rigid structure in which the 2,2′-bipyridine nitrogens are constrained in a transoid arrangement thereby discouraging metal ion coordination. Ligand **6** is more flexible and able to bind metals into a loose tetrahedral coordination pocket. It is also probable that the Cu^{II}, Ag^{I}, Pd^{II}, and Hg^{II}, which are documented to form coordination interactions with alkynes, may be binding to the alkyne substituents of the 2,2′-bipyridines of **5** and **6**.[14l,14n]

[37] Dehydrotribenzo[12]annulene, the hydrocarbon analogue of **3**, has been described to form an $[L_2Ag]^+$ complex with $AgCF_3SO_3$, in which a silver ion is sandwiched between the triangular cavities of two dehydrotribenzo[12]annulene molecules, via coordination to the alkynes. See: (a) ref 6c. (b) Ferrara, J. D.; Djebli, A.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 647. The complexation of **3** by Ag^{I} may therefore be expected to yield structurally more complex products as coordination to both the pyridine nitrogens and the alkynes is possible. However a comparison of the infrared spectra of **3** with the product of the reaction between **3** and $AgBF_4$, recorded as polychlorotrifluoroethylene mulls, showed only minor differences in the alkyne stretching absorbances. In the **3**/$AgBF_4$ reaction product, the latter absorbance appeared as a weak and broadened band at 2226 cm^{-1}, compared to two weak bands at 2227 and 2212 cm^{-1} in **3**, indicating negligible interactions between the alkyne units and Ag^{I}. However, the three strong bands due to the pyridyl CC and CN stretches at 1591, 1494, and 1410 cm^{-1} in the infrared spectrum of the **3**/$AgBF_4$ reaction product were shifted by 12, 5, and 14 cm^{-1}, respectively, to higher energy with respect to **3**, suggestive of metal ion interaction with the pyridines.

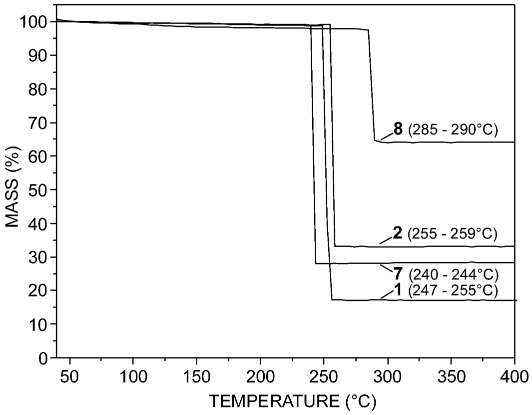

FIGURE 12. TGA thermal decomposition profiles of 2−3 mg samples of cycles **1**, **2**, **7**, and **8**, heated at a rate of 10 °C/min under nitrogen. The decomposition temperature ranges are shown in parentheses for each compound.

energy materials, igniting explosively when heated, to afford in particular cases, small quantities of buckytubes and buckyonions among other unidentified carbonaceous reaction products.[10a−d] Cycles **7** and **8** were also discovered to ignite explosively upon rapid heating above particular temperature thresholds to yield black carbon solids.[14a,c] Initial investigations into the thermal behavior of the solids described in the above work revealed that **1**, **2**, **15**, **23**, and **29** also explosively ignited with concomitant soot formation at specific temperatures. In the case of **1** and **23**, the faint odor of HCN gas was detectable directly after ignition, indicating that the reaction mechanism involves the breakdown of the pyridine rings with the expulsion of nitrogen as HCN. Thermogravimetric analyses performed upon the cycles **1**, **2**, **7**, and **8** are shown in Figure 12. The TGA decomposition temperature ranges are 5−20 °C lower than those observed using a melting point apparatus (see the Experimental Section), which may in part originate from the relatively slow thermal heat transfer properties inherent in the latter equipment. The large mass losses observed during the TGA measurements reflected the ferocity of the decompositions, which involved ejection of a portion of the sample from the crucible. The TGA heating was continued up to 900 °C for cycle **2** to assess the stability of the residue which remained after the explosive decomposition. In this case, no further changes in mass occurred until 560 °C, whereupon a relatively small and steady loss in mass was maintained up to the heating limit of 900 °C.

In contrast to the explosive decompositions described above, slow heating of the former compounds from below their respective ignition temperature thresholds, resulted in the crystals gradually becoming glossy black in appearance, but with little visible change in crystal morphology. These preliminary results suggest that *o*-diethynylpyridine-based materials may also serve as potential candidates for the generation of carbon-rich network polymers, either via a high energy explosive route, or by lower energy thermal curing. More detailed investigations into these possibilities are currently underway.

Conclusion

The above work discloses the successful synthesis and spectroscopic characterization of dehydropyridoannulenes **1**, **2**, and **3**, which constitute three structurally different members of a new class of dehydroannulenes that incorporate nitrogen heterocyclic rings. Cycles **1**−**3** possess a unique combination of features such as cyclic *ortho*-conjugation, sites for the coordination of metal ions, chirality in the case of **1**−**2**, and in particular, they were all discovered to function as fluorescent chromophores. These characteristics collectively support the conclusion that they represent structurally unique ligand scaffolds which should possess intriguing physicochemical properties. Investigations into the metal-binding profile of **3** in dilute solution demonstrated that the macrocycle functions as highly sensitive and specific sensor for Pd^{II} ions, exhibiting a fluorescence quenching output response for this metal ion. Under conditions of increased concentration, ligand **3** was found to form coordination polymers with metal ions such as Ag^{I}. Interestingly, **3** also undergoes proton triggered fluorescence quenching, in similarity to **4**−**8**.[14a,c,l,n]

In conclusion, cycles **1**−**3** and their metal complexes may be promising candidates for the development of for example, novel ion sensors, hybrid organic−inorganic coordination networks[13a−d,26a−g] and materials with photonics applications.[38a−c] Furthermore, the *o*-diethynylpyridine building blocks and macrocycle precursors described above may be expected to participate in topochemical and Bergman type polymerizations to afford novel nitrogen heterocyclic carbon rich conjugated polymers.[17b,39a,b] Reports on work supportive of the above expectations will follow, along with the preparation and properties of structurally more elaborate nitrogen heterocyclic carbon-rich materials and their metal complexes, as well as the utilization of these materials for the fabrication light emitting diodes (LEDs).

Experimental Section

General Synthetic Procedures. Variations in the following general procedures A−F were necessary in some cases in order to achieve optimal product yields and purities. These details are provided below when necessary for the particular products concerned.

(A) Sonogashira-Type Heterocouplings. To the respective iodopyridine in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ or $[PdCl_2(dppf)]\cdot CH_2Cl_2$ under an atmosphere of argon was added by syringe Et_3N or toluene as solvent, followed by the appropriate alkyne reactant. After the mixture was stirred for 0.2 h, a solution of CuI in Et_3N was syringed into the reaction and stirring continued for 5−7 days at ambient temperature in the absence of light. A gray, brown, or yellow precipitate slowly formed in all cases, visually indicating the progress of the reaction. All solvent was then removed under reduced pressure on a water bath at 70 °C and the residue extracted with 5 × 30 mL of pentane. The combined extracts were gravity filtered and the solvent removed under reduced pressure on a water bath at ambient temperature. The crude product was purified by flash chromatography on silica, eluting

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(38) The electro- and photoactive properties of structurally simple metal-complexed linear conjugated ligands have been widely studied in order to assess their potentiality for the construction of molecular level photonic devices. For reviews in this area, see: (a) De Cola, L.; Belser, P. In *Electron transfer in chemistry*; Balzani, V., Ed.; Wiley VCH: Weinheim, Germany, 2001; Vol. 5, pp 97−136. (b) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev*. **2000**, *29*, 1. (c) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev*. **1996**, *96*, 759.

(39) (a) John, J. A.; Tour, J. M. *Tetrahedron* **1997**, 15515. (b) Baldwin, K. P.; Matzger, A. J.; Scheiman, D. A.; Tessier, C. A.; Vollhardt, K. P. C.; Youngs, W. J. *Synlett* **1995**, 1215.

with CH_2Cl_2. Further purification was achieved by dissolving the product in 20−30 mL of MeOH and stirring with NORIT A decolorizing charcoal (0.05−0.25 g), gravity filtering, and removal of the solvent under reduced pressure on a water bath at 50 °C. The latter procedure was repeated using similar quantities of NORIT A and powdered anhydrous Na_2SO_4 (1−3 g) in 30−60 mL pentane and removal of the solvent under reduced pressure at ambient temperature. The product thus obtained was finally dried under dynamic vacuum at 0.01 mmHg.

(B) Selective TMS Deprotection. To a stirred solution of the trimethylsilylethynyl substrate in MeOH was added the appropriate quantity of finely powdered K_2CO_3 and the suspension stirred at ambient temperature in the absence of light for 17−36 h. The reaction solution was then reduced in volume to about 3 mL under reduced pressure on a water bath at ambient temperature and the concentrate partitioned between water (100 mL) and pentane (40 mL). The aqueous layer was extracted with a further portion of pentane (30 mL), the combined organic layers were extracted with water (5 × 30 mL) and dried (anhydrous Na_2SO_4), filtered under gravity, and the solvent was removed under reduced pressure on a water bath at ambient temperature. The product was initially purified by flash chromatography on silica with CH_2Cl_2 as eluant. The solvent was removed from the fractions containing the product, under reduced pressure on a water bath at ≤50 °C, to minimize any possible thermal degradation. Further purification was achieved by dissolving the product in 30−70 mL of MeOH and stirring with NORIT A decolorizing charcoal (0.05−0.25 g), gravity filtering, and removal of the solvent under reduced pressure on a water bath at ambient temperature. The latter procedure was repeated using similar quantities of NORIT A and powdered anhydrous Na_2SO_4 (1−3 g) in 20−50 mL of pentane and removal of the solvent under reduced pressure at ambient temperature. The product thus obtained was finally dried under dynamic vacuum at 0.01 mmHg.

(C) Hay Ethyne Homocoupling Reactions. To a solution of the arylethyne in pyridine was added a solution of the CuCl or CuI catalyst in pyridine (1−2 mL) and the stirred reaction bubbled with oxygen gas for 1.5 h. During this time, a color change from yellow to green usually occurred. The reaction flask was tightly closed and the solution vigorously stirred in the absence of light until TLC sampling indicated complete consumption of the starting alkyne (18 h to 2 d). The reaction was then poured onto a mixture of brine and water (3:1, 300 mL) and extracted with pentane (4 × 50 mL). The combined pentane extracts were washed with water (3 × 200 mL), dried (anhydrous Na_2SO_4), and filtered, and the solvent was removed under reduced pressure on a water bath at ambient temperature. The residue was further dried under dynamic vacuum over 16 h, and MeOH or MeCN (4−6 mL) was added to complete the crystallization of the product. The mixture was then triturated and briefly ultrasonicated, filtered under vacuum, and washed with a few milliliters of MeOH or MeCN. Unless otherwise stated, the product was further purified by recrystallization from MeOH (14−20 mL) and dried under dynamic vacuum at 0.01 mmHg.

(D) Fluoride-Mediated Desilylations. To a stirred solution of the trialkylsilylalkyne in THF (12−40 mL) was added dropwise a small quantity of distilled water (1−14 drops) followed by the appropriate quantity of the $[(n\text{-Bu})_4N]F$ (1.0 M in THF) solution, and stirring was continued at ambient temperature in the absence of light until TLC sampling indicated complete deprotection (14 h to 1.5 d). All solvent was removed under reduced pressure at ambient temperature, distilled water (30−50 mL) added, and the mixture filtered under vacuum. The residue collected was washed with excess distilled water and air-dried to afford a tacky solid which was purified as described individually for each compound below.

(E) Bromine/Iodine Metatheses. A dried 500 mL two-necked round-bottomed flask charged with the aryl bromide was equipped with a vacuum/argon inlet adaptor, alcohol thermometer, rubber septum, and magnetic stirrer ovoid. The flask was then evacuated and back-filled with argon four times and Et_2O (120−180 mL) added by syringe. The stirred solution was subsequently cooled to an internal temperature of −78 °C using a CO_2/acetone bath. The appropriate quantity of *n*-BuLi (1.6 M in hexanes) was added dropwise by syringe at a rate which maintained the reaction temperature between −78 and −70 °C. The reaction solution was then stirred at −78 °C for 1.5 h. Et_2O (10−30 mL) was syringed into a dried, argon-filled Schlenk tube containing diiodoethane and the mixture stirred until all of the diiodoethane dissolved. The diiodoethane solution was then added dropwise by syringe to the lithioarene reaction mixture at a rate which maintained the internal temperature between −78 and −70 °C. The reaction was stirred at −78 °C for a further 3 h and then allowed to warm to ambient temperature with continued stirring overnight. The reaction solution was extracted with distilled water (3 × 180 mL), the organic layer separated, dried (anhydrous Na_2SO_4), filtered, and the Et_2O removed by distillation at atmospheric pressure on a water bath at 50 °C. The remaining brown oil was further dried under vacuum (0.05 mmHg) and worked up as described for each compound below.

(F) Macrocyclizations to 1 and 2. In a well-ventilated hood, $[Cu_2(OAc)_4]\cdot nH_2O$ (n = 0, 2) was dissolved in warm pyridine (500−600 mL), and the stirred solution was bubbled with argon for 1.5 h, during which time it cooled to ambient temperature. A solution of the dialkyne in pyridine (**34**) or toluene (**39**) was then slowly added dropwise over 3−7 h to the $[Cu_2(OAc)_4]\cdot nH_2O$ solution, with continued stirring and argon bubbling. After the addition of the dialkyne was complete, the reaction was stirred under a static atmosphere of argon, at ambient temperature and in the absence of light for 21−25 d. All solvent was then removed under reduced pressure on a water bath, and the residue was further dried at 70 °C under vacuum for 0.5 h. Distilled water (300 mL) and excess ice were added, and the mixture was vigorously stirred. Excess solid KCN was then added in 0.2 g portions with continued stirring until no further visible change occurred, at which point the mixture appeared as a brown suspension. Further workup and purification methods are detailed separately for each product below.

3-Triisopropylsilylethynyl-4-trimethylsilylethynylpyridine (12). Compound **12** (1.414 g, 96%) was obtained as a pale yellow oil from the reaction between **11** (1.245 g, 4.13 × 10^{-3} mol), $PdCl_2(PPh_3)_2$ (0.050 g, 7.12 × 10^{-5} mol), and TIPSA (0.806 g, 4.42 × 10^{-3} mol) in Et_3N (15 mL) and a solution of CuI (0.040 g, 2.10 × 10^{-4} mol) in Et_3N (4 mL), according to the general procedure A above. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.675 (s, 1H; H2), 8.426 (d, $^3J(6,5)$ = 5.1 Hz, 1H; H6), 7.294 (d, $^3J(5,6)$ = 5.1 Hz, 1H; H5), 1.152 (s, 21H; $CH(CH_3)_2$), 0.252 ppm (s, 9H; $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 153.4, 147.8, 132.9, 125.8, 121.8, 103.9 (−C≡), 102.0 (−C≡), 100.6 (−C≡), 98.7 (−C≡), 18.7 ($CH(CH_3)_2$), 11.2 ($CH(CH_3)_2$), −0.4 ppm $Si(CH_3)_3$). IR (thin film): 3036 (w), 2959 (s), 2943 (s), 2865 (s), 2164 (m) (C≡C), 1574 (s), 1476 (s), 1463 (s), 1398 (s), 1250 (s), 874 (s), 845 (s), 679 cm^{-1} (s). FABMS: *m/z* 356 (100) [M$^+$ + H]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{21}H_{34}NSi_2$ 356.2230, found 356.2247.

3-Triisopropylsilylethynyl-4-ethynylpyridine (13). Compound **13** (2.867 g, 90%) was obtained as a soft cream crystalline solid upon the reaction between **12** (4.000 g, 1.12 × 10^{-2} mol) and K_2CO_3 (0.780 g, 5.64 × 10^{-3} mol) in MeOH (125 mL) for 1.5 d according to the general deprotection procedure B. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ = 8.706 (s, 1H; H2), 8.471 (d, $^3J(6,5)$ = 5.2 Hz, 1H; H6), 7.328 (d, $^3J(5,6)$ = 4.7 Hz, 1H; H5), 3.471 (s, 1H; −C≡CH), 1.152 ppm (s, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ = 153.0, 148.0, 132.4, 125.6, 122.7, 101.6 (−C≡), 99.4 (−C≡), 85.5 (−C≡), 79.9 (−C≡), 18.6 ($CH(CH_3)_2$), 11.2 ppm ($CH(CH_3)_2$). IR: 3151 (s) (H−C≡), 2937 (s), 2861 (s), 2165 (m) (C≡C), 2104 (s) (C≡C), 1580 (s), 1477 (s), 1461 (s), 1399 (s), 882 (s), 834 (s), 756 (s), 676 cm^{-1} (s). FABMS: *m/z* 284 (100) $[M^+ + H]$, 240 (9) $[M^+ - \{CH_2(CH_3)_2\}]$, 212 (4) $[M^+ - \{CH_2(CH_3)_2\} - 2\{CH_2\}]$, 198 (6) $[M^+ - \{CH_2(CH_3)_2\} - 3\{CH_2\}]$, 184 (9) $[M^+ - \{CH_2(CH_3)_2\} - 4\{CH_2\}]$, 170 (10) $[M^+ - \{CH_2(CH_3)_2\} - 5\{CH_2\}]$. HRMS (FAB, $[M^+ + H]$): calcd for $C_{18}H_{26}NSi$ 284.1835, found 284.1825.

1,4-Bis(4-(3-triisopropylsilylethynyl)pyridyl)buta-1,3-diyne (14). Compound **14** (0.436 g, 86%) was obtained as colorless needles from the reaction between **13** (0.510 g, 1.80×10^{-3} mol) and CuI (0.024 g, 1.26×10^{-4} mol) in oxygenated pyridine (45 mL), according to the general coupling procedure C. During workup, the crude **14** isolated from the pentane extraction was triturated in MeOH. Mp: 136.0−137.0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta = 8.733$ (s, 2H; H2), 8.510 (d, $^3J(6,5) = 5.2$ Hz, 2H; H6), 7.313 (d, $^3J(5,6) = 5.1$ Hz, 2H; H5), 1.165 ppm (m, 42H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 152.9$, 148.0, 131.7, 125.3, 122.9, 101.2 ($-C\equiv$), 100.5 ($-C\equiv$), 80.9 ($-C\equiv$), 80.2 ($-C\equiv$), 18.6 ($CH(CH_3)_2$), 11.2 ppm ($CH(CH_3)_2$). IR: 2943 (s), 2865 (s), 2155 (m) ($C\equiv C$), 1570 (s), 1471 (s), 1463 (m), 1396 (m), 996 (m), 882 (m), 833 (m), 757 (s), 673 cm^{-1} (s). FABMS: *m/z* 565 (100) $[M^+ + H]$; 521 (5) $[M^+ - \{CH_2(CH_3)_2\}]$. HRMS (FAB, $[M^+ + H]$): calcd for $C_{36}H_{49}N_2Si_2$ 565.3434, found 565.3419. Anal. Calcd for $C_{36}H_{48}N_2Si_2$: C, 76.53; H, 8.56; N, 4.96. Found: C, 76.72; H, 8.70; N, 4.90.

1,4-Bis(4-(3-ethynyl)pyridyl)buta-1,3-diyne (15). A solution of **14** (0.356 g, 6.30×10^{-4} mol), 4 drops of distilled water, and a 1.0 M solution of $[(n\text{-Bu})_4N]F$ in THF (2 mL, 2×10^{-3} mol) in THF (30 mL) were stirred for 24 h and worked up as described in the general procedure D. The crude **15** was suspended in cold MeOH (3 mL), filtered under vacuum, washed with MeOH (3×1 mL) and Et_2O (2 mL), and air-dried. The solid was then chromatographed on silica, gradient eluting successively with CH_2Cl_2, CH_2Cl_2/1%MeOH, and CH_2Cl_2/2%MeOH. Further purification was achieved by briefly stirring in CH_2Cl_2 with NORIT A (0.06 g), filtering under gravity, and removal of the solvent under reduced pressure at ambient temperature. The remaining solid was suspended in Et_2O (4 mL), filtered under vacuum, washed with cold Et_2O (2×1 mL), and air-dried to afford **15** (0.121 g, 76%) as off-white fibrous needles. (Upon slow heating from below 167.8 °C, the crystals become glossy black in appearance, with no further visible change up to 310 °C. When **15** is rapidly heated, it ignites explosively at ≥167.8 °C to yield a black residue.) ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 8.769$ (s, 2H; H2), 8.564 (d, $^3J(6,5) = 5.0$ Hz, 2H; H6), 7.402 (d, $^3J(5,6) = 5.0$ Hz, 2H; H5), 3.519 ppm (s, 2H; $-C\equiv CH$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 65 °C): $\delta = 153.4$, 148.8, 132.0, 125.6, 121.6, 84.9 ($-C\equiv$), 80.8 ($-C\equiv$), 80.1 ($-C\equiv$), 78.8 ppm ($-C\equiv$). IR: 3216 (s) ($H-C\equiv$), 3203 (s) ($H-C\equiv$), 2107 (s) ($C\equiv C$), 1574 (s), 1474 (s), 1398 (s), 1180 (m), 828 (s), 738 (s), 695 (m), 578 cm^{-1} (m). FABMS: *m/z* 253 (100) $[M^+ + H]$; HRMS (FAB, $[M^+ + H]$): calcd for $C_{18}H_9N_2$ 253.0766, found 253.0765. Anal. Calcd for $C_{18}H_8N_2$: C, 85.70; H, 3.20; N, 11.10. Found: C, 85.44; H, 3.17; N, 11.13.

3-Iodo-4-ethynylpyridine (16). A THF (18 mL) solution of **11** (0.856 g, 2.84×10^{-3} mol), distilled water (1.5 mL), and a 1.0 M solution of $[(n\text{-Bu})_4N]F$ in THF (3.0 mL, 3×10^{-3} mol) were stirred for 14 h as described in the general procedure D. The reaction solution was then diluted with water (60 mL) and extracted with pentane (3×25 mL). The combined pentane extracts were extracted with water (3×30 mL), and the organic phase was dried (anhydrous $MgSO_4$), shaken with NORIT A (0.15 g), and gravity filtered. All solvent was removed from the filtrate under reduced pressure on a water bath at ambient temperature and the remaining solid dried under dynamic vacuum to afford **16** (0.590 g, 91%) as a cream crystalline volatile solid, pure by ^{1}H and ^{13}C NMR. Mp: 86.0−87.0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta = 8.974$ (s, 1H; H2), 8.504 (d, $^3J(6,5) = 4.9$ Hz, 1H; H6), 7.377 (d, $^3J(5,6) = 4.9$ Hz, 1H; H5), 3.627 ppm (s, 1H; $-C\equiv CH$). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): $\delta = 157.2$, 148.3, 136.3, 127.2, 98.9 (C−I), 85.6 ($-C\equiv$), 82.7 ppm ($-C\equiv$). IR: 3153 (s) ($H-C\equiv$), 2097 (s) ($C\equiv C$), 1573 (s), 1460 (m), 1396 (s), 1377 (m), 1080 (m), 1016 (s), 832 (s), 785 cm^{-1} (m). EIMS: *m/z* 229 (100) $[M^+]$, 102 (29) $[M^+ - I]$. HRMS (FAB, $[M^+ + H]$): calcd for C_7H_5NI 229.9467, found 229.9468.

1,4-Bis(4-(3-iodo)pyridyl)buta-1,3-diyne (17). A solution of **16** (0.256 g, 1.12×10^{-3} mol) and CuCl (0.019 g, 1.92×10^{-4} mol) was stirred in oxygenated pyridine (18 mL) for 24 h according to the general coupling procedure C. The solvent was distilled off under vacuum at ambient temperature, and a solution of KCN (1 g) in water (20 mL) added to the residue. The mixture was stirred for 1 h and the suspended solid isolated by filtration under vacuum, washed with excess distilled water, and air-dried. The product was further purified by recrystallization from boiling heptane (20 mL), air-drying, and drying under dynamic vacuum to afford **17** (0.202 g, 79%) as colorless needles which rapidly become pink upon exposure to light. (Gradual color darkening and decomposition to a black residue occurs upon slow heating from 185 to 235 °C, with no further visible changes up to 310 °C.) ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): $\delta = 9.006$ (s, 2H; H2), 8.557 (d, $^3J(6,5) = 4.9$ Hz, 2H; H6), 7.426 ppm (d, $^3J(5,6) = 4.9$ Hz, 2H; H5). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): $\delta = 157.3$, 148.4, 135.5, 127.3, 98.8 (C−I), 83.2 ($-C\equiv$), 80.2 ppm ($-C\equiv$). IR: 2158 ($C\equiv C$) (vw), 1564 (s), 1457 (s), 1393 (m), 1276 (m), 1078 (s), 1012 (s), 831 (s), 789 (s), 560 (m), 482 cm^{-1} (m). FABMS: *m/z* 457 (100) $[M^+ + H]$. Anal. Calcd for $C_{14}H_6I_2N_2$: C, 36.87; H, 1.33; N, 6.14. Found: C, 36.55; H, 1.39; N, 6.17.

3-Bromo-4-triisopropylsilylethynylpyridine (18). Using general procedure A, a mixture of **9** (4.003 g, 1.41×10^{-2} mol), $PdCl_2(PPh_3)_2$ (0.110 g, 1.57×10^{-4} mol), and TIPSA (2.627 g, 1.44×10^{-2} mol) in Et_3N (70 mL) and a solution of CuI (0.100 g, 5.25×10^{-4} mol) in Et_3N (5 mL) was stirred at ambient temperature for 7 d. After isolation from the pentane extraction, the crude product oil was flash chromatographed on silica, eluting with Et_2O/hexane (1:4), and distilled under vacuum (122 °C/0.005 mmHg) to afford **18** (4.130 g, 87%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 8.745$ (s, 1H; H2), 8.452 (d, $^3J(6,5) = 5.0$ Hz, 1H; H6), 7.352 (d, $^3J(5,6) = 5.0$ Hz, 1H; H5), 1.152 ppm (m, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 151.7$, 147.6, 133.0, 127.1, 123.2, 102.6 ($-C\equiv$), 102.0 ($-C\equiv$), 18.6 ($CH(CH_3)_2$), 11.2 ppm ($CH(CH_3)_2$). IR (thin film): 3039 (w), 2943 (s), 2866 (s), 2164 (w) ($C\equiv C$), 1571 (s), 1465 (s), 1396 (s), 1276 (s), 1086 (s), 1020 (s), 997 (s), 883 (s), 842 (s), 705 (s), 679 (s), 663 cm^{-1} (s). FABMS: *m/z* 340 (100) $[M^+ + H]$; 296 (12) $[M^+ - \{CH_2(CH_3)_2\}]$. HRMS (FAB, $[M^+ + H]$): calcd for $C_{16}H_{25}BrNSi$ 338.0940, found 338.0941.

3-Iodo-4-triisopropylsilylethynylpyridine (19). A solution of **18** (2.600 g, 7.68×10^{-3} mol) in Et_2O (120 mL) was lithiated with 1.6 M *n*-BuLi in hexanes (5 mL, 8.00×10^{-3} mol) and the resulting pyridyllithium quenched with a solution of diiodoethane (4.40 g, 1.56×10^{-2} mol) in Et_2O (10 mL) to give crude **19** as a yellow oil, after initial workup according to the general procedure E above. The product was then column chromatographed three times in succession on silica, eluting with CH_2Cl_2, dissolved in pentane (10 mL), and gravity filtered and the pentane removed under reduced pressure on a water bath at ambient temperature to afford **19** (2.367 g, 80%) after drying under dynamic vacuum (0.01 mmHg). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 8.946$ (s, 1H; H2), 8.463 (d, $^3J(6,5) = 5.1$ Hz, 1H; H6), 7.344 (d, $^3J(5,6) = 5.1$ Hz, 1H; H5), 1.160 ppm (m, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 157.0$, 148.2, 137.4, 126.9, 105.3, 101.6, 99.2, 18.6 ($CH(CH_3)_2$), 11.2 ppm ($CH(CH_3)_2$). IR (thin film): 3034 (w), 2942 (s), 2864 (s), 2163 (w) ($C\equiv C$), 1568 (s), 1460 (s), 1394 (s), 1273 (s), 1080 (s), 1012 (s), 883 (s), 841 (s), 694 (s), 679 (s), 664 cm^{-1} (s). FABMS: *m/z* 386 (100) $[M^+ + H]$, 342 (7) $[M^+ - \{CH_2(CH_3)_2\}]$. HRMS (FAB, $[M^+ + H]$): calcd for $C_{16}H_{25}INSi$ 386.0801, found 386.0802.

3-Trimethylsilylethynyl-4-triisopropylsilylethynylpyridine (20). Using general procedure A, compound **20** (2.091 g, 96%) was obtained as a pale honey-colored oil from the reaction between **19** (2.362 g, 6.13 × 10^{-3} mol), $PdCl_2(PPh_3)_2$ (0.052 g, 7.41 × 10^{-5} mol), and TMSA (0.765 g, 7.79 × 10^{-3} mol) in Et_3N (24 mL) and a solution of CuI (0.050 g, 2.63 × 10^{-4} mol) in Et_3N (4 mL). After the chromatographic purification, the product in some runs may be contaminated with paramagnetic impurities. These may be removed by shaking a CH_2Cl_2 (30 mL) solution of the product with a mixture of powdered ascorbic acid (1 g) and KCN (1 g) followed by gravity filtration. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ = 8.684 (s, 1H; H2), 8.435 (d, $^3J(6,5)$ = 5.1 Hz, 1H; H6), 7.298 (d, $^3J(5,6)$ = 5.2 Hz, 1H; H5), 1.150 ppm (m, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ = 153.4, 148.0, 133.1, 125.8, 121.7, 102.6 (−C≡), 101.8 (−C≡), 101.1 (−C≡), 100.2 (−C≡), 18.7 ($CH(\mathit{C}H_3)_2$), 11.2 ($\mathit{C}H(CH_3)_2$), −0.2 ppm ($Si(CH_3)_3$). IR (thin film): 3036 (w), 2958 (s), 2943 (s), 2866 (s), 2165 (m) (C≡C), 1574 (s), 1475 (s), 1463 (s), 1398 (s), 1250 (s), 874 (s), 845 (s), 796 (s), 761 (s), 679 (s), 665 cm^{-1} (s). FABMS: *m/z* 356 (100) [M^+ + H]. HRMS (FAB, [M^+ + H]): calcd for $C_{21}H_{34}NSi_2$ 356.2230, found 356.2236.

3-Ethynyl-4-triisopropylsilylethynylpyridine (21). The reaction between **20** (0.451 g, 1.27 × 10^{-3} mol) and K_2CO_3 (0.090 g, 6.51 × 10^{-4} mol) in MeOH (35 mL) for 20 h afforded **21** (0.357 g, 99%) as a soft cream crystalline solid after workup, using the general deprotection procedure B. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ = 8.704 (s, 1H; H2), 8.484 (d, $^3J(6,5)$ = 5.0 Hz, 1H; H6), 7.321 (dd, $^3J(5,6)$ = 5.2 Hz, $^5J(5,2)$ = 0.8 Hz, 1H; H5), 3.377 (s, 1H; −C≡CH), 1.146 ppm (s, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ = 153.0, 148.5, 134.0, 125.4, 121.0, 102.1 (−C≡), 101.7 (−C≡), 84.0 (−C≡), 79.4 (−C≡), 18.6 ($CH(\mathit{C}H_3)_2$), 11.2 ppm ($\mathit{C}H(CH_3)_2$). IR (thin film): 3309 (s) (H−C≡), 3204 (m, broad) (H−C≡), 3038 (w), 2943 (s), 2865 (s), 2163 (w) (C≡C), 2104 (w) (C≡C), 1577 (s), 1476 (s), 1463 (s), 1399 (s), 883 (s), 857 (s), 835 (s), 764 (s), 680 (s), 666 cm^{-1} (s). FABMS: *m/z* 284 (100) [M^+ + H], 240 (8) [M^+ − {$CH_2(CH_3)_2$}], 212 (5) [M^+ − {$CH_2(CH_3)_2$} − 2{CH_2}], 198 (7) [M^+ − {$CH_2(CH_3)_2$} − 3{CH_2}], 184 (9) [M^+ − {$CH_2(CH_3)_2$} − 4{CH_2}], 170 (8) [M^+ − {$CH_2(CH_3)_2$} − 5{CH_2}]. HRMS (FAB, [M^+ + H]): calcd for $C_{18}H_{26}NSi$ 284.1835, found 284.1829.

1,4-Bis(3-(4-triisopropylsilylethynyl)pyridyl)buta-1,3-diyne (22). Compound **22** was obtained from the reaction between **21** (0.311 g, 1.10 × 10^{-3} mol) and CuCl (0.015 g, 1.52 × 10^{-4} mol) in oxygenated pyridine (29 mL), according to the general coupling procedure C. However, an additional purification step was necessary during workup. The crude **22** isolated from the pentane extraction was triturated, washed with MeCN as described in procedure C, and sublimed under vacuum (120 °C/0.01 mmHg). The sublimate was then dissolved in boiling MeOH (30 mL), NORIT A (0.05 g) added, and the mixture briefly stirred, gravity filtered, and left to stand in the dark overnight, during which time the product crystallized. A second crop of crystals were obtained upon partial evaporation of the mother liquor to afford **22** (combined yield of 0.211 g, 68%) as granular cream crystals. Mp: 131.5−132.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.699 (s, 2H; H2), 8.504 (d, $^3J(6,5)$ = 5.0 Hz, 2H; H6), 7.340 (d, $^3J(5,6)$ = 5.2 Hz, 2H; H5), 1.167 ppm (m, 42H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 153.1, 148.7, 134.5, 125.4, 120.9, 102.8 (−C≡), 101.8 (−C≡), 80.1 (−C≡), 79.0 (−C≡), 18.6 ($CH(\mathit{C}H_3)_2$), 11.2 ppm ($\mathit{C}H(CH_3)_2$). IR: 2942 (s), 2863 (s), 2164 (vw) (C≡C), 1572 (s), 1470 (s), 1397 (s), 996 (s), 880 (s), 855 (s), 832 (s), 762 (m), 679 (s), 666 (s), 642 cm^{-1} (m). FABMS: *m/z* 565 (100) [M^+ + H]. HRMS (FAB, [M^+ + H]): calcd for $C_{36}H_{49}N_2Si_2$ 565.3434, found 565.3433. Anal. Calcd for $C_{36}H_{48}N_2Si_2$: C, 76.53; H, 8.56; N, 4.96. Found: C, 76.29; H, 8.62; N, 4.96.

1,4-Bis(3-(4-ethynyl)pyridyl)buta-1,3-diyne (23). A solution of **22** (0.128 g, 2.27 × 10^{-4} mol), 5 drops of distilled water, and a 1.0 M solution of [(*n*-Bu)$_4$N]F in THF (0.6 mL, 6.0 × 10^{-4} mol) in THF (12 mL) were stirred for 18 h and worked up as described in the general procedure D. The crude **23** was suspended in cold MeOH (3 mL), filtered under vacuum, washed with MeOH (3 × 2 mL) and Et_2O (3 × 2 mL), and air-dried to afford **23** (0.055 g, 96%) as cream-colored fibrous microneedles, pure by ^{1}H and ^{13}C NMR. (Upon slow heating, the crystals become glossy black in appearance between 175 and 185 °C, with no further visible change up to 310 °C. With rapid heating, **23** ignites explosively at ≥189.0 °C to yield a black residue.) ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.792 (s, 2H; H2), 8.552 (d, $^3J(6,5)$ = 5.3 Hz, 2H; H6), 7.385 (d, $^3J(5,6)$ = 5.0 Hz, 2H; H5), 3.619 ppm (s, 2H; −C≡CH). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 153.5, 149.0, 133.2, 125.8, 120.9, 86.6 (−C≡), 79.9 (−C≡), 79.2 (−C≡), 78.7 ppm (−C≡). IR: 3205 (s) (H−C≡), 2108 (s) (C≡C), 1575 (s), 1530 (m), 1474 (m), 1401 (m), 835 (s), 752 (s), 741 (s), 721 (s), 576 cm^{-1} (m). FABMS: *m/z* 253 (100) [M^+ + H]. HRMS (FAB, [M^+ + H]): calcd for $C_{18}H_9N_2$ 253.0766, found 253.0766.

2-Trimethylsilylethynyl-3-iodopyridine (25). A solution of **24** (4.299 g, 1.69 × 10^{-2} mol) in Et_2O (180 mL) was lithiated with 1.6 M *n*-BuLi in hexanes (11 mL, 1.76 × 10^{-2} mol) and the resulting pyridyllithium quenched with a solution of diiodoethane (6.70 g, 2.38 × 10^{-2} mol) in Et_2O (30 mL) to give crude **25** as a brown oil, after initial workup according to procedure E above. The product was then chromatographed on silica, eluting initially with hexane until all the excess diiodoethane had passed from the column, and then Et_2O/hexane (1:4), to afford **25** (4.747 g, 93%) as a honey-colored oil after drying under dynamic vacuum (0.01 mmHg). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.510 (dd, $^3J(6,5)$ = 4.4 Hz, $^4J(6,4)$ = 0.9 Hz, 1H; H6), 8.110 (dd, $^3J(4,5)$ = 8.2 Hz, $^4J(4,6)$ = 1.2 Hz, 1H; H4), 6.933 (dd, $^3J(5,4)$ = 8.2 Hz, $^3J(5,6)$ = 4.7 Hz, 1H; H5), 0.295 ppm (s, 9H; ($Si(CH_3)_3$)). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 148.7, 147.1, 145.9, 123.7, 104.6, 99.6, 98.6, −0.5 ppm ($Si(CH_3)_3$). IR (thin film): 2959 (s), 2167 (m) (C≡C), 1558 (s), 1407 (s), 1262 (s), 1250 (s), 1008 (s), 867 (s), 845 (s), 760 cm^{-1} (s). FABMS: *m/z* 302 (100) [M^+ + H]. HRMS (FAB, [M^+ + H]): calcd for $C_{10}H_{13}INSi$ 301.9862, found 301.9873.

2-Trimethylsilylethynyl-3-triisopropylsilylethynylpyridine (26). Using general procedure A, a mixture of **25** (1.008 g, 3.35 × 10^{-3} mol), $PdCl_2(PPh_3)_2$ (0.046 g, 6.55 × 10^{-5} mol), and TIPSA (0.732 g, 4.01 × 10^{-3} mol) in Et_3N (15 mL) and a solution of CuI (0.040 g, 2.10 × 10^{-4} mol) in Et_3N (5 mL) was heated in a bath at 75 °C for 3 d. The heating ensured complete conversion of **25**, as the reaction was found to be rather sluggish when conducted at ambient temperature. The crude product was chromatographed three times (silica/CH_2Cl_2) and further purified as described in general procedure A above to yield **26** (0.760 g, 64%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.483 (dd, $^3J(6,5)$ = 4.8 Hz, $^4J(6,4)$ = 1.6 Hz, 1H; H6), 7.748 (dd, $^3J(4,5)$ = 7.9 Hz, $^4J(4,6)$ = 1.8 Hz, 1H; H4), 7.165 (dd, $^3J(5,4)$ = 7.9 Hz, $^3J(5,6)$ = 4.7 Hz, 1H; H5), 1.151 (s, 21H; $CH(CH_3)_2$), 0.263 ppm (s, 9H; $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 148.6, 144.4, 140.1, 122.8, 122.1, 102.6 (−C≡), 102.4 (−C≡), 98.60 (−C≡), 98.56 (−C≡), 18.7 ($CH(\mathit{C}H_3)_2$), 11.2 ($\mathit{C}H(CH_3)_2$), −0.3 ppm ($Si(CH_3)_3$). IR (thin film): 3039 (w), 2957 (s), 2943 (s), 2865 (s), 2163 (m) (C≡C), 2149 (m, sh) (C≡C), 1463 (s), 1444 (s), 1415 (s), 1250 (s), 1177 (s), 1100 (s), 883 (s), 845 (s), 800 (s), 786 (s), 768 (s), 678 (s), 666 (s), 636 cm^{-1} (s). FABMS: *m/z* 356 (100) [M^+ + H], 312 (6) [M^+ − {$CH_2(CH_3)_2$}], 270 (9) [M^+ − {$CH_2(CH_3)_2$} − 3{CH_2}]. HRMS (FAB, [M^+ + H]): calcd for $C_{21}H_{34}NSi_2$ 356.2230, found 356.2240.

2-Ethynyl-3-triisopropylsilylethynylpyridine (27). A solution of **26** (0.657 g, 1.85 × 10^{-3} mol) in MeOH (40 mL) with K_2CO_3 (0.130 g, 9.41 × 10^{-4} mol) was stirred for 17 h at ambient temperature. The reaction was worked up according to the general deprotection procedure B with omission of the chromatography step to afford **27** (0.519 g, 99%) as a very pale yellow oil that crystallized at −30 °C and remelted upon warming to ambient temperature. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.50 (dd, $^3J(6,5)$ = 4.8 Hz, $^4J(6,4)$ = 1.6 Hz, 1H; H6), 7.768 (dd, $^3J(4,5)$ = 7.9 Hz, $^4J(4,6)$ = 1.4 Hz, 1H; H4), 7.215 (dd, $^3J(5,4)$ = 7.9 Hz, $^3J(5,6)$ = 4.7 Hz, 1H; H5), 3.331 (s, 1H; −C≡CH), 1.148 ppm (s, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 148.6, 144.3, 139.5, 123.6, 122.5, 102.2 (−C≡), 99.0 (−C≡), 81.6 (−C≡), 80.8 (−C≡), 18.6 ($CH(CH_3)_2$), 11.2 ppm ($CH(CH_3)_2$). IR (thin film): 3309 (s) (H−C≡), 3217 (m, broad) (H−C≡), 3041 (w), 2943 (s), 2865 (s), 2160 (m) (C≡C), 2109 (m) (C≡C), 1549 (m), 1463 (s), 1444 (m), 1414 (s), 1099 (s), 997 (m), 883 (s), 861 (m), 802 (m), 769 (s), 748 (s), 678 (s), 662 (s), 639 cm^{-1} (s). FABMS: *m/z* 284 (100) [$M^+ + H$], 240 (8) [$M^+ - \{CH_2(CH_3)_2\}$], 212 (3) [$M^+ - \{CH_2(CH_3)_2\} - 2\{CH_2\}$], 198 (4) [$M^+ - \{CH_2(CH_3)_2\} - 3\{CH_2\}$]. HRMS (FAB, [$M^+ + H$]): calcd for $C_{18}H_{26}NSi$ 284.1835, found 284.1828.

1,4-Bis(2-(3-triisopropylsilylethynyl)pyridyl)buta-1,3-diyne (28). Compound **28** (0.296 g, 65%) was obtained as colorless acicular plates from the reaction between **27** (0.459 g, 1.62×10^{-3} mol) and CuCl (0.019 g, 1.92×10^{-4} mol) in oxygenated pyridine (30 mL), according to the general coupling procedure C. During workup, the crude **28** isolated from the pentane extraction was triturated in MeCN. Mp: 158.0−159.6 °C. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.521 (dd, $^3J(6,5)$ = 4.8 Hz, $^4J(6,4)$ = 1.6 Hz, 2H; H6), 7.769 (dd, $^3J(4,5)$ = 7.9 Hz, $^4J(4,6)$ = 1.7 Hz, 2H; H4), 7.223 (dd, $^3J(5,4)$ = 7.9 Hz, $^3J(5,6)$ = 5.0 Hz, 2H; H5), 1.146 ppm (s, 42H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 148.8, 143.9, 139.4, 124.4, 122.6, 101.8 (−C≡), 100.0 (−C≡), 80.8 (−C≡), 76.8 (−C≡), 18.6 ($CH(CH_3)_2$), 11.2 ppm ($CH(CH_3)_2$). IR: 3043 (w), 2960 (s), 2942 (s), 2891 (s), 2864 (s), 2160 (m) (C≡C), 2148 (m, sh) (C≡C), 1462 (m), 1403 (s), 1242 (s), 1099 (s), 994 (s), 882 (s), 750 (s), 677 (s), 662 (s), 640 cm^{-1} (s). FABMS: *m/z* 565 (100) [$M^+ + H$]. HRMS (FAB, [$M^+ + H$]): calcd for $C_{36}H_{49}N_2Si_2$ 565.3434, found 565.3419. Anal. Calcd for $C_{36}H_{48}N_2Si_2$: C, 76.53; H, 8.56; N, 4.96. Found: C, 76.26; H, 8.63; N, 4.90.

1,4-Bis(2-(3-ethynyl)pyridyl)buta-1,3-diyne (29). A solution of **28** (0.246 g, 4.35×10^{-4} mol), 2 drops of distilled water, and a 1.0 M solution of [$(n\text{-Bu})_4N$]F in THF (1.5 mL, 1.5×10^{-3} mol) in THF (30 mL) were stirred for 1.5 d and worked up as described in the general procedure D. The crude product, which was found to be soluble in MeOH and MeCN, was dissolved in Et_2O (400 mL), NORIT A (0.08 g) added, the mixture briefly stirred then gravity filtered, and the solvent removed under reduced pressure on a water bath at ambient temperature. The product was further purified by chromatography on silica eluting with CH_2Cl_2 and then suspended in Et_2O/pentane (15 mL, 1:1) and filtered under vacuum. The collected solid was washed with Et_2O/pentane (2 × 2 mL, 1:1) and air-dried to afford **29** (0.072 g, 65%) as photosensitive white fibrous microneedles, pure by ^1H and ^{13}C NMR. (Upon slow heating from below 164.0 °C, the crystals become glossy black in appearance, with no further visible change up to 310 °C. With rapid heating, **29** ignites explosively at ≥164.0 °C to yield a black residue.) ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.571 (dd, $^3J(6,5)$ = 5.0 Hz, $^4J(6,4)$ = 1.4 Hz, 2H; H6), 7.806 (dd, $^3J(4,5)$ = 7.9 Hz, $^4J(4,6)$ = 1.5 Hz, 2H; H4), 7.268 (dd, $^3J(5,4)$ = 7.9 Hz, $^3J(5,6)$ = 4.7 Hz, 2H; H5) 3.501 ppm (s, 2H; −C≡CH). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 149.5, 144.0, 139.7, 123.3, 122.9, 84.9 (−C≡), 80.4 (−C≡), 79.0 ppm (−C≡). ^{13}C NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ = 150.3, 144.2, 140.4, 123.8, 123.7, 85.2 (−C≡), 81.1 (−C≡), 79.6 (−C≡), 76.4 ppm (−C≡). IR: 3210 (s) (H−C≡), 3068 (w), 2106 (m) (C≡C), 1412 (s), 1099 (m), 808 (s), 763 cm^{-1} (s). FABMS: *m/z* 253 (100) [$M^+ + H$]. HRMS (FAB, [$M^+ + H$]): calcd for $C_{18}H_9N_2$ 253.0766, found 253.0772.

2-Ethynyl-3-iodopyridine (30). A THF (40 mL) solution of **25** (1.187 g, 3.94×10^{-3} mol), distilled water (1.0 mL), and a 1.0 M solution of [$(n\text{-Bu})_4N$]F in THF (4.1 mL, 4.1×10^{-3} mol) were stirred for 20 h as described in the general procedure D. All solvent was removed from the reaction under reduced pressure on a water bath at ambient temperature, water (30 mL) added, and the emulsion extracted with Et_2O (3 × 20 mL). The combined organic extracts were extracted with water (5 × 30 mL), dried (anhydrous Na_2SO_4), and filtered, and the solvent was removed under reduced pressure on a water bath at ambient temperature. The product was further purified by chromatography on silica, eluting with CH_2Cl_2, and then dissolved in boiling hexane (15 mL), gravity filtered, and the solvent removed under reduced pressure on a water bath at ambient temperature to afford **30** (0.690 g, 76%) after drying under vacuum (ambient temperature/0.01 mmHg) as a pungent-smelling pale yellow oil. ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ = 8.549 (dd, $^3J(6,5)$ = 4.7 Hz, $^4J(6,4)$ = 1.5 Hz, 1H; H6), 8.139 (dd, $^3J(4,5)$ = 8.1 Hz, $^4J(4,6)$ = 1.5 Hz, 1H; H4), 6.996 (dd, $^3J(5,4)$ = 8.0 Hz, $^3J(5,6)$ = 4.6 Hz, 1H; H5), 3.417 ppm (s, 1H; −C≡CH). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ = 148.9, 146.5, 146.1, 124.2, 98.1 (C−I), 83.8 (−C≡), 80.9 ppm (−C≡). IR (thin film): 3286 (s) (H−C≡), 3207 (s, broad) (H−C≡), 3039 (m), 2112 (s) (C≡C), 1561 (s), 1542 (s), 1429 (s), 1408 (s), 1123 (s), 1061 (s), 1009 (s), 793 (s), 752 (s), 657 (s), 645 cm^{-1} (s). FABMS: *m/z* 230 (100) [$M^+ + H$]. HRMS (FAB, [$M^+ + H$]): calcd for C_7H_5IN 229.9467, found 229.9472.

1-[3-(4-Trimethylsilylethynyl)pyridyl]-2-[3-(4-triisopropylsilylethynyl)pyridyl]ethyne (31). Using general procedure A, a mixture of **11** (0.478 g, 1.59×10^{-3} mol), **21** (0.387 g, 1.37×10^{-3} mol), and $PdCl_2(PPh_3)_2$ (0.042 g, 5.98×10^{-5} mol) in Et_3N (20 mL) and a solution of CuI (0.040 g, 2.10×10^{-4} mol) in Et_3N (2.5 mL) were stirred at ambient temperature for 5 d. The crude product was chromatographed (silica/CH_2Cl_2) and then rechromatographed on a fresh silica column, eluting first with CH_2Cl_2 followed by CH_2Cl_2/3%MeOH and further purified by treatment with NORIT A in pentane to yield **31** (0.466 g, 75%) as a pale honey-colored oil. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.782 (s, 1H; 4-triisopropylsilylethynylpyridine H2), 8.725 (s, 1H; 4-trimethylsilylethynylpyridine H2), 8.502 (d, $^3J(6,5)$ = 5.0 Hz, 2H; 4-triisopropylsilylethynylpyridine/4-trimethylsilylethynylpyridine H6), 7.378 (d, $^3J(5,6)$ = 5.3 Hz, 1H; 4-triisopropylsilylethynylpyridine H5), 7.351 (d, $^3J(5,6)$ = 5.3 Hz, 1H; 4-trimethylsilylethynylpyridine H5), 1.121 (s, 21H; $CH(CH_3)_2$), 0.257 ppm (s, 9H; $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 152.8, 152.3, 148.52, 148.50, 133.3, 133.1, 125.8, 125.2, 121.5, 121.4, 105.1 (−C≡), 102.3 (−C≡), 102.0 (−C≡), 100.4 (−C≡), 91.9 (−C≡), 91.3 (−C≡), 18.6 ($CH(CH_3)_2$), 11.2 ($CH(CH_3)_2$), −0.3 ppm $Si(CH_3)_3$). IR (thin film): 3036 (w), 2957 (s), 2943 (s), 2892 (s), 2865 (s), 2162 (m) (C≡C), 1574 (s), 1485 (s), 1470 (s), 1407 (s), 1251 (s), 883 (s), 861 (s), 838 (s), 802 (s), 761 (s), 679 (s), 666 cm^{-1} (s). FABMS: *m/z* 457 (100) [$M^+ + H$], 413 (12) [$M^+ - \{CH_2(CH_3)_2\}$]. HRMS (FAB, [$M^+ + H$]): calcd for $C_{28}H_{37}N_2Si_2$ 457.2495, found 457.2496.

1-[3-(4-Ethynyl)pyridyl]-2-[3-(4-triisopropylsilylethynyl)pyridyl]ethyne (32). A solution of **31** (0.442 g, 9.68×10^{-4} mol) in MeOH (27 mL) with K_2CO_3 (0.070 g, 5.06×10^{-4} mol) was stirred for 20 h at ambient temperature. The reaction was worked up according to the general deprotection procedure B except that the product was chromatographed by elution on silica with CH_2Cl_2 followed by CH_2Cl_2/3% MeOH. The column was best shielded from direct light due to the enhanced photosensitivity of **32**. After the chromatographic purification, the product was directly dried under dynamic vacuum to afford **32** (0.337 g, 91%) as a colorless viscous oil that partly crystallized upon storage at −30 °C. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.798 (d, $^5J(2,5)$ = 0.6 Hz, 1H; 4-triisopropylsilylethynylpyridine H2), 8.761 (d, $^5J(2,5)$ = 0.6 Hz, 1H; 4-ethynylpyridine H2), 8.538 (d, $^3J(6,5)$ = 5.2 Hz, 1H; 4-ethynylpyridine H6), 8.510 (d, $^3J(6,5)$ = 5.0 Hz, 1H; 4-triisopropylsilylethynylpyridine H6), 7.404 (dd, $^5J(5,2)$ = 0.6 Hz, $^3J(5,6)$ = 5.3 Hz, 1H; 4-ethynylpyridine H5), 7.375 (dd, $^5J(5,2)$ = 0.7 Hz, $^3J(5,6)$ = 5.1 Hz, 1H; 4-triisopropylsilylethynylpyridine H5), 3.569 (s, 1H; −C≡CH), 1.116 ppm (m, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 153.0, 152.4, 148.6, 133.1, 132.3, 125.8, 125.7, 121.8, 121.2, 102.3 (−C≡), 102.0 (−C≡), 92.0 (−C≡), 90.8 (−C≡), 86.2 (−C≡), 79.5 (−C≡), 18.6 ($CH(CH_3)_2$), 11.1 ppm ($CH(CH_3)_2$). IR (thin film): 3302 (m) (H−C≡), 3197 (m, broad) (H−C≡), 3037 (w), 2943 (s), 2890 (s), 2865 (s), 2107 (m) (C≡C), 1578 (s), 1485 (s), 1463 (s), 1407 (s), 878 (s), 831 (s), 771 (s), 679 (s), 665 (s), 643 cm^{-1} (s). FABMS: *m/z* 385 (100) [$M^+ + H$]. HRMS (FAB, [$M^+ + H$]): calcd for $C_{25}H_{29}N_2Si$ 385.2100, found 385.2105.

1,4-bis[4-(3-{2,1-ethynediyl-3-(4-triisopropylsilylethynyl)pyridyl})pyridyl]buta-1,3-diyne (33) (from 32). Compound **33** (0.248 g, 77%) was obtained as cream-colored flakes from the reaction between **32** (0.322 g, 8.37×10^{-4} mol) and CuCl (0.010 g, 1.01×10^{-4} mol) in oxygenated pyridine (30 mL), according to the general coupling procedure C. During workup, the crude **33** isolated from the pentane extraction was triturated in MeOH. Mp: 140.5−142.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 8.835$ (d, $^5J(2,5) = 0.9$ Hz, 2H; 4-triisopropylsilylethynylpyridine H2), 8.778 (d, $^5J(2,5) = 0.9$ Hz, 2H; bis[4-pyridyl]butadiyne H2), 8.569 (d, $^3J(6,5) = 5.0$ Hz, 2H; bis[4-pyridyl]butadiyne H6), 8.499 (d, $^3J(6,5) = 5.3$ Hz, 2H; 4-triisopropylsilylethynylpyridine H6), 7.455 (dd, $^5J(5,2) = 0.9$ Hz, $^3J(5,6) = 5.3$ Hz, 2H; bis[4-pyridyl]butadiyne H5), 7.366 (dd, $^5J(5,2) = 0.9$ Hz, $^3J(5,6) = 5.2$ Hz, 2H; 4-triisopropylsilylethynylpyridine H5), 1.118 ppm (m, 42H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 153.1$, 152.5, 148.7, 148.6, 133.1, 131.3, 125.8, 125.7, 122.1, 121.0, 102.2 (−C≡), 102.1 (−C≡), 93.0 (−C≡), 90.5 (−C≡), 81.0 (−C≡), 80.3 (−C≡), 18.6 ($CH(\mathit{C}H_3)_2$), 11.1 ppm ($\mathit{C}H(CH_3)_2$). UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 244 (sh) (73950), 251 (76457), 301 (32749), 312 (32098), 354 (23406), 375 nm (sh) (11535 M^{-1} cm^{-1}). Fluorescence emission ([**33**] ≤ 3.0×10^{-5} M in CH_2Cl_2; 353 nm excitation): λ_{max} = 393, 414 nm (sh). IR: 2942 (s), 2864 (s), 2164 (vw) (C≡C), 2151 (w) (C≡C), 1576 (s), 1484 (s), 1403 (s), 879 (s), 831 (s), 774 (s), 678 (s), 666 (s), 577 cm^{-1} (m). FABMS: *m/z* 767 (100) [M^+ + H], 723 (11) [M^+ − {$CH_2(CH_3)_2$}]. HRMS (FAB, [M^+ + H]): calcd for $C_{50}H_{55}N_4Si_2$ 767.3965, found 767.3980. Anal. Calcd for $C_{50}H_{54}N_4Si_2$: C, 78.28; H, 7.10; N, 7.30. Found: C, 78.10; H, 7.11; N, 7.16.

1,4-bis[4-(3-{2,1-ethynediyl-3-(4-triisopropylsilylethynyl)pyridyl})pyridyl]buta-1,3-diyne (33) (from 15 + 19). A mixture of **15** (0.100 g, 3.96×10^{-4} mol) and [$PdCl_2$(dppf)]·CH_2Cl_2 (0.016 g, 1.96×10^{-5} mol) in toluene (16 mL, N_2 bubbled) under argon was briefly heated until all the suspended **15** had dissolved. The stirred reaction was then placed in a bath at 60 °C, and a solution of **19** (0.406 g, 1.05×10^{-3} mol) and CuI (0.015 g, 7.88×10^{-5} mol) in Et_3N (1.5 mL) were added consecutively via syringe. The reaction was monitored by TLC sampling, which indicated that the **15** had been consumed by 22 h. The solvent was then removed under reduced pressure on a hot water bath and the residue chromatographed first on alumina (neutral, activity II/III) with CH_2Cl_2 and CH_2Cl_2/1% MeOH, followed by elution on alumina (basic, activity III/IV) with CH_2Cl_2. The product was thus obtained as a clear glass, which crystallized after addition of MeOH (4 mL) and brief heating. Filtration of the cooled mixture under vacuum and washing the collected solid with MeOH, followed by air-drying and further drying under dynamic vacuum, afforded **33** (0.146 g, 48%) as colorless microflakes. Mp: 142.0−142.8 °C. Anal. Calcd for $C_{50}H_{54}N_4Si_2$: C, 78.28; H, 7.10; N, 7.30. Found: C, 78.04; H, 7.13; N, 7.09.

1,4-bis[4-(3-{2,1-ethynediyl-3-(4-ethynyl)pyridyl})pyridyl]buta-1,3-diyne (34). A solution of **33** (0.258 g, 3.36×10^{-4} mol), 14 drops of distilled water, and a 1.0 M solution of [$(n\text{-}Bu)_4N$]F in THF (0.9 mL, 9.0×10^{-4} mol) in THF (33 mL) were stirred for 20 h and worked up as described in the general procedure D. The crude **34** was suspended in MeOH (20 mL), homogenized by brief stirring, and then filtered under vacuum, washed with MeOH (5 × 2 mL), Et_2O (3 × 2 mL), and air-dried to afford **34** (0.150 g, 99%) as an amorphous white solid, pure by ^{1}H and ^{13}C NMR. The product was obtained as analytically pure microcrystalline needles upon recrystallization from boiling toluene, to which NORIT A (0.07 g) had been added prior to gravity filtration. Mp: upon slow heating, the crystals become glossy black-brown in appearance between 195 and 225 °C, with no further visible change up to 320 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 8.864$ (s, 2H; bis[4-pyridyl]butadiyne H2), 8.840 (s, 2H; 4-ethynylpyridine H2), 8.593 (d, $^3J(6,5) = 5.3$ Hz, 2H; bis[4-pyridyl]butadiyne H6), 8.499 (d, $^3J(6,5) = 5.0$ Hz, 2H; 4-ethynylpyridine H6), 7.457 (d, $^3J(5,6) = 5.2$ Hz, 2H; bis[4-pyridyl]butadiyne H5), 7.322 (d, $^3J(5,6) = 5.0$ Hz, 2H; 4-ethynylpyridine H5), 3.694 (s, 2H; −C≡CH). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 153.0$, 152.8, 148.9, 148.8, 132.2, 131.0, 125.8, 125.7, 121.9, 121.4, 92.3 (−C≡), 91.1 (−C≡), 86.6 (−C≡), 81.2 (−C≡), 80.6 (−C≡), 79.4 ppm (−C≡). UV/vis (CH_2Cl_2): λ_{max} nm (ϵ) = 247 (68678), 284 (36704), 317 (34602), 348 (25819), 374 nm (sh) (12082 M^{-1} cm^{-1}). Fluorescence emission ([**34**] ≤ 4.4×10^{-5} M in CH_2Cl_2; 350 nm excitation): λ_{max} = 391, 414 nm (sh). IR: 3292 (s) (H−C≡), 3204 (s) (H−C≡), 3029 (w), 2214 (w) (C≡C), 2116 (w) (C≡C), 2104 (m) (C≡C), 1579 (s), 1570 (s), 1411 (s), 841 (s), 822 (s), 642 (s), 573 cm^{-1} (s). FABMS: *m/z* 455 (100) [M^+ + H]. HRMS (FAB, [M^+ + H]): calcd for $C_{32}H_{15}N_4$ 455.1297, found 455.1290. Anal. Calcd for $C_{32}H_{14}N_4$: C, 84.57; H, 3.11; N, 12.33. Found: C, 84.22; H, 2.96; N, 12.27.

Dehydrotetrapyrido[20]annulene (1). To a stirred solution of [$Cu_2(OAc)_4$]·$2H_2O$ (2.320 g, 5.81×10^{-3} mol) in pyridine (600 mL) was added a hot solution of **34** (0.132 g, 2.90×10^{-4} mol) in pyridine (25 mL) over 3 h. The reaction was stirred for 21 d, the solvent removed, and the residue treated with aqueous KCN as described in general procedure F above. The aqueous suspension was then extracted with warm $CHCl_3$ (200 mL) and the emulsion filtered through a G2 frit under gentle vacuum. The dried solid collected and the aqueous portion of the filtrate were each further extracted with $CHCl_3$ (2 × 100 mL). All organic extracts were combined and gravity filtered and the solvent removed by distillation on a water bath to afford crude **1**, which was chromatographed twice on alumina (neutral, activity II/III) eluting first with CH_2Cl_2 and finally CH_2Cl_2/1%MeOH. The columns must be shielded from direct light due to the enhanced photosensitivity of the product. The solid thus obtained was dissolved in boiling toluene (6 mL) and gravity filtered, the solvent removed under reduced pressure on a water bath, and MeCN (2 mL) added. The suspension was briefly stirred and filtered under vacuum and the collected solid washed with MeCN (3 × 0.5 mL), air-dried, and further dried under vacuum (70 °C/0.01 mmHg) to afford **1** (0.053 g, 40%) as colorless microneedles (pure by ^{1}H and ^{13}C NMR). (Slow heating from below 267.5 °C up to 310 °C causes the crystals to become glossy black in appearance. Upon rapid heating, **1** explosively ignites at ≥267.5 °C to yield a glossy black residue.) ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 8.834$ (s, 4H; H2), 8.570 (d, $^3J(6,5) = 5.0$ Hz, 4H; H6), 7.419 ppm (d, $^3J(5,6) = 5.2$ Hz, 4H; H5). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 152.0$ (C2), 148.8 (C6), 132.0, 125.8 (C5), 121.5, 91.5 (−C≡), 81.2 (−C≡), 80.1 ppm (−C≡). UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 256 (119963), 268 (129267), 294 (sh) (34713), 318 (28478), 333 (sh) (24193), 354 nm (sh) (12429 M^{-1} cm^{-1}). Fluorescence emission ([**1**] ≤ 8.8×10^{-5} M in CH_2Cl_2; 330 nm excitation): λ_{max} = 443 nm. IR: 3033 (vw), 2219 (vw) (C≡C), 2158 (w) (C≡C), 2142 (w) (C≡C), 1570 (s), 1481 (m), 1468 (m), 1416 (m), 826 (s), 801 cm^{-1} (m). FABMS: *m/z* 453 (100) [M^+ + H]. HRMS (FAB, [M^+ + H]): calcd for $C_{32}H_{13}N_4$ 453.1140, found 453.1140.

1-[2-(Trimethylsilylethynylphenyl)]-2-[3-(4-triisopropylsilylethynyl)pyridyl]ethyne (36). Using general procedure A, a mixture of **21** (0.502 g, 1.77×10^{-3} mol), **35** (0.562 g, 1.87×10^{-3} mol), and $PdCl_2(PPh_3)_2$ (0.051 g, 7.27×10^{-5} mol) in toluene (18 mL) and a solution of CuI (0.052 g, 2.73×10^{-4} mol) in Et_3N (4 mL) were stirred at ambient temperature for 6 d. The crude **36** thus obtained was chromatographed (silica/CH_2Cl_2), redissolved in CH_2Cl_2 (30 mL), and vigorously shaken with a mixture of powdered ascorbic acid (1 g) and KCN (1 g) followed by gravity filtration in order to remove the accompanying paramagnetic impurities. The product was then dissolved in MeCN (40 mL), NORIT A (0.2 g) added, the mixture briefly stirred and gravity filtered, and the solvent removed under reduced pressure on a water bath at ambient temperature. Further drying under dynamic vacuum (0.01 mmHg/12 h) afforded **36** (0.625 g, 77%) as a pale honey-colored viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 8.789$ (s, 1H; pyridine H2), 8.475 (d, $^3J(6,5) = 5.2$ Hz, 1H; pyridine H6), 7.507 (m, 2H; phenyl H3/6), 7.374 (d, $^3J(5,6) =$

5.0 Hz, 1H; pyridine H5), 7.291 (m, 2H; phenyl H4/5), 1.121 (m, 21H; CH(CH_3)$_2$), 0.237 ppm (s, 9H; Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 152.5, 147.6, 133.2, 132.2, 131.8, 128.5, 128.0, 126.0, 125.9, 125.3, 122.2, 103.2 (−C≡), 102.5 (−C≡), 101.9 (−C≡), 99.3 (−C≡), 94.9 (−C≡), 88.8 (−C≡), 18.6 (CH(CH_3)$_2$), 11.2 (CH(CH_3)$_2$), −0.05 ppm Si(CH_3)$_3$). IR (thin film): 3060 (w), 2943 (s), 2892 (s), 2865 (s), 2221 (w) (C≡C), 2160 (s) (C≡C), 1574 (s), 1485 (s), 1464 (s), 1443 (s), 1399 (s), 1250 (s), 882 (s), 833 (s), 798 (s), 758 (s), 679 (s), 665 (s), 643 cm^{-1} (s). FABMS: *m/z* 456 (100) [M$^+$ + H], 412 (18) [M$^+$ − {CH_2(CH_3)$_2$}]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{29}H_{38}NSi_2$ 456.2543, found 456.2547.

1-[2-(Ethynylphenyl)]-2-[3-(4-triisopropylsilylethynyl)-pyridyl]ethyne (37). A solution of **36** (0.604 g, 1.33 × 10^{-3} mol) in MeOH (35 mL) with K_2CO_3 (0.097 g, 7.02 × 10^{-4} mol) was stirred for 1.5 d at ambient temperature. The reaction was worked up as described in the general deprotection procedure B (with omission of the step involving treatment with NORIT A in MeOH) to afford **37** (0.447 g, 88%) as a light honey-colored oil. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.799 (s, 1H; pyridine H2), 8.475 (d, $^3J(6,5)$ = 5.2 Hz, 1H; pyridine H6), 7.537 (m, 2H; phenyl H3/6), 7.368 (d, $^3J(5,6)$ = 5.0 Hz, 1H; pyridine H5), 7.328 (m, 2H; phenyl H4/5), 3.352 (s, 1H; −C≡CH), 1.118 ppm (m, 21H; CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 152.7, 147.8, 133.2, 132.6, 131.9, 128.5, 128.4, 125.8, 125.6, 124.9, 122.1, 102.5 (−C≡), 101.8 (−C≡), 94.3 (−C≡), 89.0 (−C≡), 81.9 (−C≡), 81.6 (−C≡), 18.6 (CH(CH_3)$_2$), 11.2 ppm (CH(CH_3)$_2$). IR (thin film): 3304 (m) (H−C≡), 3216 (w, broad) (H−C≡), 3060 (w), 2942 (s), 2890 (s), 2864 (s), 2221 (w) (C≡C), 2162 (w) (C≡C), 2104 (w) (C≡C), 1574 (s), 1486 (s), 1463 (s), 1399 (s), 876 (s), 826 (s), 758 (s), 679 (s), 665 cm^{-1} (s). FABMS: *m/z* 384 (100) [M$^+$ + H], 340 (7) [M$^+$ − {CH_2(CH_3)$_2$}]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{26}H_{30}NSi$ 384.2148, found 384.2147.

1,4-bis[2-{2,1-ethynediyl-3-(4-triisopropylsilylethynyl)-pyridyl}phenyl]buta-1,3-diyne (38). A solution of **37** (0.427 g, 1.11 × 10^{-3} mol) and CuCl (0.013 g, 1.31 × 10^{-4} mol) in oxygenated pyridine (30 mL) was stirred at ambient temperature for 48 h according to the general coupling procedure C. The crude **38** was isolated from the pentane extraction as an oil which did not crystallize upon drying under vacuum or treatment with MeOH and MeCN. The product was therefore flash chromatographed on silica, gradient eluting successively with CH_2Cl_2, CH_2Cl_2/1% MeOH, and CH_2Cl_2/3% MeOH. Compound **38** (0.402 g, 94%) was thus isolated as a viscous honey-colored oil which hardened into a glass after drying under dynamic vacuum overnight. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.862 (s, 2H; pyridine H2), 8.459 (d, $^3J(6,5)$ = 5.3 Hz, 2H; pyridine H6), 7.602 (m, 2H; phenyl H6), 7.523 (m, 2H; phenyl H3), 7.337 (m, 6H; pyridine H5, phenyl H4/5), 1.121 ppm (m, 42H; CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 153.0, 147.9, 133.1, 133.0, 132.0, 128.7, 128.6, 126.2, 125.7, 124.6, 121.9, 102.6 (−C≡), 101.6 (−C≡), 94.1 (−C≡), 89.7(−C≡), 81.2 (−C≡), 78.0 (−C≡), 18.6 (CH(CH_3)$_2$), 11.2 ppm (CH(CH_3)$_2$). UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 239 (82687), 253 (82599), 290 (34950), 322 (sh) (33331), 344 (28592), 367 nm (16393 M^{-1} cm^{-1}). Fluorescence emission ([**38**] ≤ 2.7 × 10^{-5} M in CH_2Cl_2; 345 nm excitation): λ_{max} = 379, 397, 409 nm (sh). IR: 3058 (w), 2943 (s), 2890 (s), 2864 (s), 2165 (w) (C≡C), 1571 (s), 1484 (s), 1464 (s), 1445 (s), 1399 (s), 876 (s), 826 (s), 757 (s), 680 (s), 663 cm^{-1} (s). FABMS: *m/z* 765 (100) [M$^+$ + H], 721 (12) [M$^+$ − {CH_2(CH_3)$_2$}]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{52}H_{57}N_2Si_2$ 765.4060, found 765.4047.

1,4-bis[2-{2,1-ethynediyl-3-(4-ethynyl)pyridyl}phenyl]-buta-1,3-diyne (39). A THF (40 mL) solution of **38** (0.393 g, 5.14 × 10^{-4} mol), 10 drops of distilled water, and a 1.0 M solution of [(*n*-Bu)$_4$N]F in THF (1.4 mL, 1.4 × 10^{-3} mol) were stirred for 24 h and worked up as described in the general procedure D. The crude product was suspended in MeOH (30 mL), homogenized by brief ultrasonication, filtered under vacuum, washed with excess MeOH, and air-dried to afford **39** (0.211 g, 91%) as a cream-colored solid, pure by ^{1}H and ^{13}C NMR. The product was further purified for elemental analysis by three recrystallizations from toluene as microrectangular plates. (Upon slow heating, the crystals become glossy black-brown in appearance between 180 and 215 °C, with no further visible change up to 320 °C.) ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.834 (d, $^5J(2,5)$ = 0.6 Hz, 2H; pyridine H2), 8.446 (d, $^3J(6,5)$ = 5.3 Hz, 2H; pyridine H6), 7.612 (m, 4H; phenyl H3/6), 7.379 (m, 4H; phenyl H4/5), 7.285 (dd, $^3J(5,6)$ = 5.0 Hz, $^5J(5,2)$ = 0.6 Hz, 2H; pyridine H5), 3.760 ppm (s, 2H; −C≡CH). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 152.8, 148.2, 133.2, 132.6, 132.0, 129.1, 128.8, 126.0, 125.6, 124.2, 122.2, 94.4 (−C≡), 89.2 (−C≡), 86.6 (−C≡), 81.6 (−C≡), 79.5 (−C≡), 78.4 ppm (−C≡). UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 240 (73777), 259 (sh) (53736), 286 (40376), 317 (36925), 343 (26925), 368 nm (13932 M^{-1} cm^{-1}). Fluorescence emission ([**39**] ≤ 3.5 × 10^{-5} M in CH_2Cl_2; 344 nm excitation): λ_{max} = 378, 397, 407 nm (sh). IR: 3180 (s) (H−C≡), 2103 (s) (C≡C), 1581 (s), 1486 (s), 1438 (s), 1402 (s), 1377 (s), 832 (s), 771 (s), 752 (s), 722 (s), 578 cm^{-1} (s). FABMS: *m/z* 453 (100) [M$^+$ + H]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{34}H_{17}N_2$ 453.1392, found 453.1387. Anal. Calcd for $C_{34}H_{16}N_2$: C, 90.25; H, 3.56; N, 6.19. Found: C, 89.84; H, 3.77; N, 6.05.

Dehydrodibenzodipyrido[20]annulene (2). To a stirred solution of anhydrous $Cu_2(OAc)_4$ (2.909 g, 8.01 × 10^{-3} mol) in pyridine (500 mL) was added a hot solution of **39** (0.181 g, 4.00 × 10^{-4} mol) in toluene (100 mL) over 7 h. The reaction was stirred for 25 d, the solvent removed, and the residue treated with aqueous KCN as described in general procedure F above. The aqueous suspension was filtered under vacuum and the collected solid washed with excess distilled water and air-dried. The solid was briefly ultrasonicated and boiled in CH_2Cl_2 (50 mL) and the suspension chromatographed on silica, gradient eluting with CH_2Cl_2/*n*% MeOH (*n* = 1, 3, 5, and 10). The crude **2** thus obtained was suspended in MeCN (10 mL), briefly ultrasonicated, isolated by filtration under vacuum, washed with MeCN (3 × 1 mL), and chromatographed on alumina (neutral, activity II/III), eluting with CH_2Cl_2. Product **2** was then redissolved in CH_2Cl_2 (10 mL) and gravity filtered and the solvent removed by distillation on a water bath. The product was finally resuspended in MeCN (10 mL), briefly ultrasonicated, filtered under vacuum, washed with MeCN (3 × 2 mL), and air-dried to afford **2** (0.142 g, 79%) as a white microcrystalline solid (pure by ^{1}H and ^{13}C NMR). (Slow heating from below 264.0 °C up to 310 °C induces the crystals to become glossy black in appearance. Upon rapid heating, **2** explosively ignites at ≥264.0 °C to yield a glossy black residue.) ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.796 (d, $^5J(2,5)$ = 0.6 Hz, 2H; pyridine H2), 8.511 (d, $^3J(6,5)$ = 5.3 Hz, 2H; pyridine H6), 7.568 (m, 4H; phenyl H3/6), 7.391 (dd, $^3J(5,6)$ = 5.1 Hz, $^5J(5,2)$ = 0.9 Hz, 2H; pyridine H5), 7.355 ppm (m, 4H; phenyl H4/5). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): δ = 151.9 (pyridine C2), 148.1 (pyridine C6), 133.3 (phenyl C3/6), 132.0, 131.7 (phenyl C3/6), 128.94 (phenyl C4/5), 128.86 (phenyl C4/5), 125.7 (pyridine C5), 125.6, 125.1, 122.4, 94.9 (−C≡), 88.2 (−C≡), 81.3 (−C≡), 81.0 (−C≡), 80.2 (−C≡), 78.0 ppm (−C≡). UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 255 (122058), 269 (125936), 298 (32802), 315 (26045), 353 nm (sh) (10162 M^{-1} cm^{-1}). Fluorescence emission ([**2**] ≤ 9.8 × 10^{-5} M in CH_2Cl_2; 318 nm excitation): λ_{max} = 456 nm. IR: 3054 (w), 2218 (w) (C≡C), 2158 (w) (C≡C), 1574 (s), 1483 (s), 1467 (s), 1446 (m), 1411 (m), 1402 (m), 839 (m), 825 (s), 796 (m), 764 (s), 746 (m), 578 cm^{-1} (m). FABMS: *m/z* 451 (100) [M$^+$ + H]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{34}H_{15}N_2$ 451.1235, found 451.1228.

(2-Iodophenylethynyl)triisopropylsilane (41). A solution of **40** (4.743 g, 1.41 × 10^{-2} mol) in Et_2O (160 mL) was lithiated with 1.6 M *n*-BuLi in hexanes (11 mL, 1.76 × 10^{-2} mol) and the resulting phenyllithium quenched with a solution of diiodoethane (5.637 g, 2.00 × 10^{-2} mol) in Et_2O (20 mL) to give crude **41** as a brown oil, after initial workup according to procedure E above. However, in this case, the phenyllithium solution was stirred at −78 °C for 0.7 h, allowed to warm to 0 °C over 0.5 h, and recooled to −78 °C prior to quenching to ensure complete lithiation. The product was purified by distillation under vacuum (130−133 °C/0.005 mmHg) to afford **41** (4.455 g, 82%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 7.836$ (dd, $^3J(3,4) = 7.9$ Hz, $^4J(3,5) = 0.9$ Hz, 1H; H3), 7.492 (dd, $^3J(6,5) = 7.8$ Hz, $^4J(6,4) = 1.6$ Hz, 1H; H6), 7.280 (td, $^3J(5,4/5,6) = 7.3$ Hz, $^4J(5,3) = 1.2$ Hz, 1H; H5), 6.984 (td, $^3J(4,3/4,5) = 7.7$ Hz, $^4J(4,6) = 1.8$ Hz, 1H; H4), 1.167 ppm (m, 21H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 138.7$, 133.2, 130.2, 129.3, 127.6, 108.0, 100.8, 95.4 (−C≡), 18.7 ($CH(CH_3)_2$), 11.4 ppm ($CH(CH_3)_2$). IR (thin film): 3062 (w), 2941 (s), 2890 (s), 2863 (s), 2159 (s) (C≡C), 1460 (s), 1429 (m), 1017 (s), 996 (m), 883 (s), 831 (s), 753 (s), 678 (s), 667 (s), 634 cm^{-1} (m).

1,4-bis[4-(3-{2,1-ethynediyl-2-(triisopropylsilylethynylphenyl)})pyridyl]buta-1,3-diyne (42). A mixture of **15** (0.156 g, 6.18×10^{-4} mol), **41** (0.594 g, 1.55×10^{-3} mol), and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (0.027 g, 3.31×10^{-5} mol) in toluene (25 mL, N_2 bubbled) under argon was briefly heated until all the suspended **15** dissolved. The stirred reaction was then placed in a bath at 60 °C and a solution of CuI (0.026 g, 1.37×10^{-4} mol) in Et_3N (1.5 mL) added via syringe. Stirring and heating were maintained for 24 h, by which time TLC of the reaction indicated that all of the **15** had been consumed. All solvent was then removed under reduced pressure on a hot water bath and the residue chromatographed first on alumina (neutral, activity II/III) with CH_2Cl_2, followed by gradient elution on silica with CH_2Cl_2/1% MeOH and finally CH_2Cl_2/3% MeOH. The product was further purified by treatment with NORIT A in pentane and drying under vacuum, as described in the general procedure A, to afford **42** (0.225 g, 48%) as a clear pale brown tacky glass. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta =$ 8.776 (d, $^5J(2,5) = 0.9$ Hz, 2H; pyridine H2), 8.529 (d, $^3J(6,5) = 5.2$ Hz, 2H; pyridine H6), 7.543 (m, 2H; phenyl H3), 7.490 (m, 2H; phenyl H6), 7.399 (dd, $^3J(5,6) = 5.2$ Hz, $^5J(5,2) = 0.9$ Hz, 2H; pyridine H5), 7.230 (m, 4H; phenyl H4/5), 1.124 ppm (m, 42H; $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C): $\delta = 152.4$, 148.0, 132.8, 132.7, 131.4, 128.7, 128.1, 125.9, 125.6, 124.7, 122.9, 104.9 (−C≡), 96.4 (−C≡), 95.8 (−C≡), 87.8 (−C≡), 81.0 (−C≡), 80.4 (−C≡), 18.7 ($CH(CH_3)_2$), 11.3 ppm ($CH(CH_3)_2$). UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 237 (sh) (81152), 245 (85222), 297 (31819), 312 (28127), 356 nm (20025 M^{-1} cm^{-1}). Fluorescence emission ([**42**] $\leq 5.2 \times 10^{-5}$ M in CH_2Cl_2; 355 nm excitation): $\lambda_{max} = 417$ nm. IR ($CHCl_3$ evapd thin film): 3058 (w), 2942 (s), 2890 (s), 2864 (s), 2216 (w) (C≡C), 2156 (m) (C≡C), 1570 (s), 1485 (s), 1463 (s), 1442 (m), 883 (s), 873 (m), 827 (m), 767 (s), 757 (s), 678 (s), 662 (s), 639 cm^{-1} (m). FABMS: *m/z* 765 (100) [M$^+$ + H]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{52}H_{57}N_2Si_2$ 765.4060, found 765.4064.

3-Iodo-4-Cu(I)pyridylacetylide (43). A solution of $CuSO_4\cdot 5H_2O$ (0.79 g, 3.16×10^{-3} mol) in 28% aq ammonia (5.2 mL) and distilled water (14 mL) was bubbled with argon for 0.25 h. $NH_2OH\cdot HCl$ (0.44 g, 6.33×10^{-3} mol) was then added, causing the reaction to decolorize with effervescence. With continued argon bubbling and vigorous stirring, a solution of **16** (0.719 g, 3.14×10^{-3} mol),in EtOH (20 mL) was added dropwise. The resulting thick orange suspension was stirred for a further 24 h, distilled water (20 mL) added, and the mixture filtered under vacuum, washed with excess distilled water, EtOH, and Et_2O, and dried under vacuum at ambient temperature to yield **43** (0.867 g, 95%) as an amorphous brown-red solid. IR: 2019 (w), 1953 (m), 1922 (s), 1573 (s), 1568 (s), 1453 (s), 1399 (m), 1271 (m), 1078 (m), 1024 (m), 827 (m), 726 cm^{-1} (m). Caution!: copper acetylides present explosive hazards and should never be heated while dry.

Dehydrotripyrido[12]annulene (3). A homogeneous suspension of **43** (0.810 g, 2.78×10^{-3} mol) in pyridine (52 mL) was refluxed at 145 °C for 18 h, during which time the color of the suspension changed from orange-brown to black. The bulk of the solvent was then removed under reduced pressure on a water bath. Concentrated aq KCN solution (30 mL) was added to the black residue and the mixture heated to 90 °C then stirred at ambient temperature for 0.7 h and extracted with $CHCl_3$ (5 × 60 mL). The combined $CHCl_3$ extracts were dried (anhydrous Na_2SO_4) and filtered, the solvent was distilled off under reduced pressure, and MeOH (10 mL) was added to the residue. The mixture was filtered under vacuum and the isolated solid twice chromatographed on alumina (basic, activity IV) eluting with CH_2Cl_2. The product thus obtained was suspended in acetone (3 mL), filtered under vacuum, washed with acetone (2 × 1 mL), and air-dried to afford **3** (0.013 g, 5%) as a pale yellow fibrous solid. Mp: >350 °C (the product changes color to dark brown at ≥312 °C with no observable melting). After the $CHCl_3$ extraction above, an insoluble amorphous black solid (0.226 g; IR: 2191 (m) (C≡C), 1594 (s), 831 cm^{-1} (m)) was isolated from the aqueous suspension upon filtration under vacuum, washing with excess dist. water, EtOH and air-drying. Characterization data for **3**: ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C; [**3**] = 3.3×10^{-2} M): $\delta = 8.589$ (s, 3H; H2), 8.472 (d, $^3J(6,5) = 5.1$ Hz, 3H; H6), 7.231 ppm (d, $^3J(5,6) = 5.2$ Hz, 3H; H5). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C; [**3**] = 3.3×10^{-2} M): $\delta = 152.8$ (C2), 150.0 (C6), 134.3, 124.9 (C5), 121.5, 94.4 (−C≡), 92.7 ppm (−C≡). UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 272 (82387), 279 (84060), 288 (172135), 308 (10148), 319 (12802), 330 (14653), 343 nm (19448 M^{-1} cm^{-1}). Fluorescence emission ([**3**] $\leq 4.5 \times 10^{-5}$ M in CH_2Cl_2, 288 nm excitation): $\lambda_{max} = 474$, 494, 524 nm. IR: 3028 (s), 2227 (m) (C≡C), 2212 (m) (C≡C), 1579 (s), 1489 (s), 1396 (s), 1377 (s), 848 (s), 838 (s), 585 cm^{-1} (s). FABMS: *m/z* 304 (100) [M$^+$ + H]. HRMS (FAB, [M$^+$ + H]): calcd for $C_{21}H_{10}N_3$ 304.0875, found 304.0880.

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Supporting Information Available: General experimental methods and ^{1}H and ^{13}C spectra of **1**−**3**, **12**−**13**, **16**, **18**, **25**−**27**, **29**−**32**, **36**−**38**, **41**, and **42**. This material is available free of charge via the Internet at http://pubs.acs.org.

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