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Ag^I-Directed Triple-Stranded Helicates with meta-Ethynylpyridine Ligands

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A series of triple-stranded complexes, $[1a_3Ag]BF_4$, $\label{eq:additional} \textbf{[1b}_3Ag]BF_4, \ \textbf{[2a}_3Ag_2](BF_4)_2, \ \textbf{[2b}_3Ag_2](BF_4)_2, \ \text{and} \ \textbf{[3}_3Ag_3] (BF_4)_3$, have been obtained through the self-assembly of Ag^I ions with *p*-phenylene ethynylpyridine ligands. X-ray crystallographic studies unambiguously demonstrated a Ag^I-directed monodentate triple-stranded helical structure in the

Introduction

Helical structures are ubiquitous in biological molecules such as protein, DNA, and collagens.^[1] In the past few decades, a great deal of effort has been devoted to the design and synthesis of artificial molecules that are able to mimic biomacromolecules both structurally and functionally. The research has led to a good level of understanding of the relationship between structures and functions as well as the self-assembly processes involved in biomacromolecule formation, and the work ultimately led to the discovery of foldamers.^[2] Helicates, which are an intensively studied class of foldamers, are oligonuclear metal complexes in which two or more linear organic oligodonor ligands wrap around a series of metal ions in a helical fashion.^[3] Because significant attention has been paid to the self-assembly of polynuclear helicates in recent years, huge progress has been made in this area.^[4-11] Among these helicates, ligands that are composed of strands are classified according to their coordination centers, for example, oligonitrogen donors (oligopyridine, imine, five-membered azaheterocycles),^[4a] oligooxygen donors (catecholato group),^[5] mixed oxygen/

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solid state for 1b and 2b. A combination of NMR spectroscopy, HRMS (ESI), and isothermal titration microcalorimetry studies further confirmed that strands 1, 2, and 3 are also able to form triple-stranded helical structures in the presence of Aq^I ions in solution.

nitrogen donors (8-hydroxyquinoline derivatives),^[4a,4b] as well as sulfur or phosphorus donors (benzene-o-dithiolato group).^[6] These ligands selectively coordinate with diverse metal ions to form a variety of novel triple-stranded helicates. The preference of the oligooxygen donors to coordinate some alkali metal ions^[7] (e.g., Li⁺, Na⁺, K⁺) has led to efficacious templated synthesis of triple-stranded structures. For instance, N-oxide binaphthol derived ligands wrap around three independent Na⁺ or Li⁺ ions to form helicates.^[7a] trinuclear triple-stranded Additionally, recent studies demonstrated that transition-metal ions [Co(II/III),^[8a,8c,8d] Ga^{III},^[8c] In^{III},^[8c] Fe(II/III),^[8d–8h] Cu(I/II),^[8h,8i,10] Zn^{II} ,^[8b,8j,8k] Mn^{II} ,^[8k,8l] $Ag^{I[9i,11]}$ and Ln^{III[8b,9]} (Ln = La, Eu, Ce, Tb, Lu) also play a very important role in the formation of triple-stranded helicates. The metallo centers in the helicates impart a cationic charge, which is expected to enhance the potential use of such triple-stranded helicates in chemical and biochemical domains, particularly, in DNA labeling and recognition.^[8d,9d] It is noteworthy that almost all of the ligands in the triplestranded helicates are bidentate, tridentate, or even multidentate.^[7–9] In contrast, there are few reports on metal-directed monodentate triple-stranded helicates,^[10,11] in particular, Ag^I-mediated monodentate triple-stranded helicates.^[11] The group of Piguet reported an infinite, linear, triple-stranded helicate polymer in the solid state, which consisted of lanthanide helicates and AgI ions. However, Ag^I ions served as a bridge connecting two adjacent lanthanide helicates so as to form the polymers.^[9i] The silver ion was, in fact, a cofactor for the formation of the triple helicate polymers but was not a crucial factor for the formation of individual triple helicates in Piguet's system. In this paper, we designed and synthesized a novel monodentate triple-stranded helicate in which Ag^I acts as a crucial directing agent.



It is well established that pyridine is a suitable donor due to the strength of the metal-nitrogen coordination bond in some supramolecular architectures such as cages^[12] and foldamers.^[4,10,13-16a] A survey of CCDC data shows that Ag^I and pyridine are able to form many complexes with different stoichiometries up to 1:4, which inspired us to design Ag^I-mediated monodentate triple-stranded helicates by carefully controlling the stoichiometry of Ag^I and pyridine. In this work, we report a series of strands consisting of pphenylene ethynylpyridine ligands that possess a Ag^I-coordination site at each pyridine unit (Figure 1 and Scheme S1). We hypothesized that novel monodentate triple-stranded helicates could be achieved due to the steric bulk of the 2,6-diethynyl-pyridine ligand. A methylene group was inserted in two p-phenylene ethynylpyridine ligands as a hinge in the long strands to relax the rigidity of the long triple-stranded helicates. After screening a variety of arrays of the benzene and pyridine rings in the strand,



Figure 1. Structures of ligands 1-3.

we concluded that strands with three or less pyridine rings gave rise to effective and stable metal complexes, i.e., triplestranded helicates. In contrast, strands with four or more pyridines resulted in the formation of insoluble complexes. In addition, we introduced *n*-butyl groups at both ends of the ligands to enhance the solubility of the ligand in organic solvents.

Results and Discussion

Synthesis and Characterization of the Ligands

The synthetic procedures for ligands 1-3 are shown in Scheme 1. Starting from 4,4'-methylenedianiline, the diiodide derivative bis(4-iodophenyl)methane (4) was synthesized by diazo reaction.^[21] The Sonogashira coupling reaction of 4 with trimethylsilylacetylene in the presence of diisopropylamine, catalyzed by tetrakis(triphenylphosphine)palladium and cuprous iodide, gave 5 in 83% yield, which was subsequently ethynylated by tetrabutylammonium fluoride in dichloromethane to give diacetylene 6 in 95% yield. Commercially available 2,6-dibromopyridine was subjected to Sonogashira reaction with 2.5 or 0.2 equiv. of (trimethylsilyl)acetylene (TMSA) to yield 7 and 9, respectively, which was followed by treatment with tetrabutylammonium fluoride to generate diacetylene 8 (92% yield) and monoacetylene 10 (88% yield), respectively. The monomeric strand of 1a and 1b were synthesized by the coupling reaction of diacetylene 8 with 1-butyl-4-iodobenzene and iodo-



Scheme 1. Synthetic route to ligands 1-3.



benzene, in yields of 90 and 81%, respectively. Monoacetylene 10 was allowed to react with 1-butyl-4-iodobenzene and iodobenzene, producing 11a and 11b in 86 and 84% yield, respectively. The Sonogashira coupling of bromides 11a-b with diacetylene 6 afforded the dimeric strand of 2a (80% yield) and **2b** (91% yield). Sonogashira reaction and ethynylation converted bromide 11a into acetylide 13. The reaction of diacetylene 8 with an excess of diiodide derivative 4 gave 14 in 72% yield. Finally, the trimeric strand of 3 was obtained by the Sonogashira coupling reaction of diiodide 14 with acetylide 13. All intermediates of the monomers, dimers and trimer were purified by column chromatography and characterized on the basis of ¹H and ¹³C NMR spectroscopy, mass spectra, and melting point measurements. Furthermore, 1D-NOEDIF, 2D 1H-1H COSY and ROESY spectra were recorded to identify the signals of the protons of 1-3 and the protons of the corresponding Ag^I complexes (see Figure S2–S9 in the Supporting Information).

Solid-State Characterization of 1b and 2b

Various attempts to obtain crystals of the Ag^I complexes of **1a** and **2a** that were suitable for X-ray diffraction analysis were unsuccessful, probably due to the disorder of the butyl moiety. Fortunately, crystals of complexes of **1b** and **2b** without a butyl moiety were obtained for X-ray diffraction analysis.

Crystals of the Ag^I complex of **1b** were achieved by slow evaporation from an ethanol/H₂O solution. The head-tohead three-stranded helicate crystallized as a racemate in the trigonal system with the space group R3c, and both left and right helicates are present in the solid state, as shown in Figure 2 and Table S1. The Ag^I ion is coordinated by three pyridyl groups from three ligands, in which each pyridyl moiety acts as a monodentate ligand. Each threestranded helicate has a C_3 axis. The three nitrogen atoms and the Ag^I ion display a trigonal planar geometry, which is uncommon in comparison to the reported Ag^I-pyridine complexes, $^{[14,15]}$ with a Ag–N distance of 2.248(6) Å and a chelate angle of approximately $119.72(3)^{\circ}$. BF₄⁻ is bound by six C-H groups from three different ligands through six hydrogen bonds.^[8g] Clearly, all six C-H···F bonds point to the same F atom (F2), which sits at the C_3 axis (C···F distance 3.370-3.418 Å, average 3.394 Å and C-H···F angles 123.07-126.07°, average 124.57°). It is worth mentioning that one of the terminal benzene rings (labeled as C) interacts with one of the pyridine rings (labeled as B) (Figure S18) at the adjacent ligands in a nearly parallel orientation, with a dihedral angle about 161.02° and a interplanar distance of approximately 4.599 Å (centroid to centroid), suggesting the existence of weak π ··· π interactions.^[17a,17b] These C–H···F bonds and π ··· π interactions may also play important roles in the stabilization of the helicate.

Crystals of the Ag^I complex of **2b** were obtained by slow evaporation from a mixed solvent of $CHCl_3$ and ethanol. The X-ray crystallographic analysis explicitly indicated that



Figure 2. X-ray crystal structure of Ag^I complex of **1b**. Upper: stick diagrams; lower: space-filling diagrams; left: side view; right: top view. In both diagrams, alternate ligands are colored separately, C, H: red, blue and green for different strands; N: pink; Ag: light blue, counterions have been omitted for clarity.

[2b₃Ag₂](BF₄)₂ adopted a head-to-head triple-stranded dinuclear helical structure with a C_3 -symmetric axis passing through the Ag^I ions, as shown in Figure 3. The threestranded helicate crystallized as a racemate in the trigonal system with the space group R3 (Table S1). Three strands of 2b, each containing two coordinated sites, wrap around two Ag^I ions with Ag1–Ag2 distance of 14.882 Å between the two coordination sites, and each three pyridyl groups bridge one Ag^I atom in a monodentate model. The three nitrogen atoms and AgI ion exhibit a trigonal planar geometry, in which the Ag–N distance is in the range of 2.242(3) to 2.247(3) Å and the corresponding chelate angles are approximately 119.68(15) to 119.99(3)°. The dihedral angle between adjacent methylene-bridged benzene rings C and D is about 101.9°. Notably, there are three C-H groups participating in the C-H···F type hydrogen bonds with one counterion BF₄⁻ (C···F distance 3.333 Å, and C-H···F angle 130.88°). The distance between C5 and the corresponding phenyl ring A in the adjacent ligand is about 3.884 Å, with a dihedral angle between the two phenyl rings of about 116.02°, indicating a slight C-H··· π interaction



Figure 3. X-ray crystal structures of the Ag^I complex of **2b**. Upper: stick diagrams; lower: space-filling diagrams; left: side view; right: top view. In both diagrams, alternate ligands are coloured separately, C, H: red, blue and green for different strands; N: pink; Ag: light blue, counterions have been omitted for clarity.



(Figure S19).^[17b,17c] Similar C–H··· π interactions were also observed between other carbon atoms and the corresponding aromatic rings (e.g., C17···benzene ring C, distance 3.818 Å, C1···pyridyl ring B, distance 3.945 Å, C39···pyridyl ring E, distance 3.761 Å). All of these C–H···F bonds and slight C–H··· π interactions may play a significant role in stabilizing the helicate.

Having found that triple-stranded helicates were present in the solid state, the coordination behavior of these ligands in solution was then investigated on the basis of ¹H NMR spectra, HRMS (ESI) and isothermal titration microcalorimetry (ITC) measurements.

NMR Titration Studies

¹H NMR titration experiments with monomeric strand **1a** and Ag^{I} ions were performed in $[D_{6}]$ acetone at room temperature (Figure 4, a). The spectra showed a simple pattern containing one set of signals, which suggested a rapid equilibrium was established on the NMR timescale, presumably due to labile Ag^I ions involved in the coordination process.^[16b] No further significant changes occurred when the number of equivalents of AgI ions was increased above 1.5, whereupon the coordination and dissociation of Ag^I complex achieved dynamic equilibrium (Figure S10). Upon increasing the amount of AgI ions, the chemical shifts of the pyridyl moiety displayed a clear downfield shift because coordination occurred between the pyridyl moiety and the Ag^I ions.^[13b] The pyridyl proton peaks H_a and H_b at δ = 7.87 and 7.59 ppm moved to $\delta = 8.17$ and 7.88 ppm, respectively. The changes of chemical shifts were up to $\Delta \delta = 0.30$ and 0.29 ppm for H_a and H_b , respectively. In contrast, the chemical shifts of the aromatic protons H_c and H_d on the terminal benzene rings displayed little variation (δ = 7.46 ppm, $\Delta \delta = -0.10$ ppm and $\delta = 7.24$ ppm, $\Delta \delta =$ -0.08 ppm, respectively).

¹H NMR titration studies of **2a** and **3** were performed in the mixed solvent of CDCl3 and [D6]acetone to improve their solubility (Figure S11–S12). Upon addition of Ag^I ions into a solution of dimeric strand 2a, the chemical shifts of all aromatic protons experienced similar variations to that of **1a** (Figure 4, b), suggesting that coordination took place between pyridine units and Ag^I ions. The changes in the chemical shifts were saturated upon addition of 1.2 equiv. of Ag^{I} ions (Figure S11). In detail, the H_{a}^{*} peak of the pyridine units at $\delta = 8.25$ ppm displayed a remarkable downfield shift with $\Delta \delta = 0.48$ ppm. As for H_b* and H_c^* , its chemical shift appeared as a doublet at δ = 7.56 ppm in the free strand. The titrations of Ag^I ions induced the signals of H_b^* and H_c^* to split into two sets of doublet peaks at δ = 7.96 and 7.91 ppm with significant downfield shifts of $\Delta \delta = 0.40$ and 0.35 ppm, respectively. In addition, the other protons H_d^* , H_e^* , H_f^* , H_g^* of the phenyl rings ($\delta_{\text{Hd}*}$ = 7.10 ppm, $\Delta \delta$ = -0.13 ppm; $\delta_{\text{He}*}$ = 7.32 ppm, $\Delta \delta = -0.20$ ppm; $\delta_{\text{Hf}^*} = 7.34$ ppm, $\Delta \delta =$ -0.18 ppm; $\delta_{\text{Hg}*} = 6.99$ ppm, $\Delta \delta = -0.28$ ppm) and H_h* of the methylene linker ($\delta = 3.96$ ppm, $\Delta \delta = -0.10$ ppm) shifted



Figure 4. Partial ¹H NMR spectra of **1a**, **2a** and **3** and the corresponding Ag^I complex at 298 K: (a) **1a** (upper) and **1a**/Ag (1:2) (lower) in [D₆]acetone, 400 MHz; (b) **2a** (upper) and **2a**/Ag (1:2) (lower) in CDCl₃/[D₆]acetone (3:2, v/v), 400 MHz; (c) **3** (upper) and **3**/Ag (1:2) (lower) in CDCl₃/[D₆]acetone (9:1, v/v), 500 MHz. [**1a**] = [**2a**] = [**3**] = 2.0 mM; * represent solvent peaks.

to high field (Figure 4, b). These upfield shifts originate from the shielding effect of the corresponding phenyl rings of the counterpart strands in the triple helicates.^[16a]

The titration of trimeric strand 3 showed a set of relatively complex ¹H NMR spectra in the absence of Ag^I ions, due to the presence of a variety of aromatic rings. However, upon the addition of 1 equiv. of Ag^I ions into a solution of trimeric strand 3, the ¹H NMR spectrum became simple and clear, indicating the formation of the Ag^I complex of **3** (Figure 4, c and Figure S12). The most evident changes were observed in the signals of the pyridyl proton. In detail, the peaks $H_{a'}$ at $\delta = 8.19$ ppm and $H_{i'}$ at $\delta = 8.15$ ppm showed significant downfield shifts of $\Delta \delta = 0.55$ and 0.51 ppm, which exhibited two sets of triplet peaks in the complex but an apparent single triplet in the free strand. Similar changes were observed for H_b' , H_h' and H_j' with $\Delta \delta = 0.48, 0.48, \text{ and } 0.36 \text{ ppm}$, respectively. Simultaneously, the signals split into two sets of doublet peaks at $\delta = 7.89$ and 7.77 ppm in the complex. Other aromatic protons experienced diverse upfield shifts, as expected. For example, the aromatic protons $H_{k'}$ at $\delta = 7.23$ ppm and $H_{l'}$ at $\delta =$ 7.00 ppm shifted to high field with $\Delta \delta = -0.23$ and -0.12 ppm, respectively. The aromatic protons H_c', H_d', H_{f} , and H_{g} also experienced moderate upfield shifts ($\Delta \delta$ from -0.22 to -0.28 ppm).

HRMS (ESI) Analysis

To determine the stoichiometry of the complexes in solution, HRMS (ESI) were recorded for the Ag^I complexes of **1a** and **2a** (Figure 5, Figure S13 and S14 in the Supporting Information). The mass spectrometric studies with **1a** showed a major peak at m/z 1282.59 that was assigned to



the $[1a_3Ag]^+$ complex (Figure 5, a). Two other peaks at m/z 783.47 and 891.36, assigned to $[1a_2H]^+$ and $[1a_2Ag]^+$,



Figure 5. Positive HRMS (ESI) of the Ag^I complexes for 1a and 2a. (a) The Ag^I complex of 1a: (upper) showing the experimented signal of $[1a_3Ag]^+$ at m/z 1282.59; (lower) The calculated signal of $[1a_3Ag]^+$ (b) The Ag^I complex of 2a: (upper) showing the experimented signal of $[2a_3Ag_2]^{2+}$ at m/z 1131.91; (lower) The calculated signal of $[2a_3Ag_2]^{2+}$.

respectively, were also observed under the same experimental conditions (Figure S13). The coexistence of $[\mathbf{1a}_2H]^+$ and $[\mathbf{1a}_2Ag]^+$ species, together with the $[\mathbf{1a}_3Ag]^+$ complex, indicated that a dynamic equilibrium involving a series of solution species occurred, as observed in other reported systems.^[16b,18] However, the observation of a major peak at m/z 1282.59 for $[\mathbf{1a}_3Ag]^+$ illustrated a 3:1 stoichiometry for the $\mathbf{1a}/Ag^{\mathrm{I}}$ complex was the dominant coordination mode in solution.^[18a]

Similar behavior was observed for the Ag^I complex of **2a**. Here, the base peak at m/z 1131.91 was assigned to the expected twofold charged 3:2 complex $[2a_3Ag_2]^{2+}$, which showed that Ag^I ions indeed formed dinuclear triple-stranded complex with **2a** in solution (Figure 5, b). Other signals at m/z 790.24 and 1473.58 were observed with low intensity for two bimetallic complexes with two and four strands, respectively $[(2a_2Ag_2)^{2+}$ and $(2a_4Ag_2)^{2+}$, Figure S14]. These results revealed that the 3:2 binding stoichiometry for the complex formed by **2a** and Ag^I ions was also the dominant coordination mode in solution.^[18b] For the Ag^I complex of **3**, no featured peaks were detected, presumably because of the poor solubility of the complex in polar solvents such as acetonitrile and methanol used in the ESI experiments.

Isothermal Titration Calorimetry (ITC) Experiments

ITC is a powerful tool for investigating the thermodynamics of small molecule/metal coordination systems. The exothermic or endothermic heat that is evolved during a reaction can be directly measured by ITC to determine a binding equilibrium constant (β) and an enthalpy change (ΔH^0) for the reaction. Entropy changes ($T\Delta S^0$) can also be calculated (Figure S15–S17).^[19,20] Another benefit of ITC is that the binding stoichiometry of certain complexation



Figure 6. ITC profile for the titration of ligands 1a, 2a, and 3 with $AgBF_4$ at 298 K. (Upper) Raw ITC data; each peak corresponds to the thermal power evolved from the solution of ligand on addition of aliquots of $AgBF_4$ solution. (Lower) Normalized titration curve; the red solid line represents the best-fit curve obtained from the assumed stoichiometry.



events can be easily determined from the inflection point in the titration curve plotting heat versus the molar ratio of metal ion to ligand.^[20a]

ITC experiments with **1a** and Ag^{I} ions was performed in ethanol, and ITC experiments of **2a** and **3** were performed in a mixed solvent of chloroform and ethanol to improve their solubility (Figure 6); the data are listed in Table 1. The molar ratios of Ag^{I} ions to **1a**, **2a** and **3** were 0.34 ± 0.001 , 0.70 ± 0.04 , and 0.83 ± 0.001 , respectively, corresponding to stoichiometries of 1:3, 2:3, and 3:3 for Ag^{I} complexes of **1a**, **2a** and **3**. These results were consistent with the observations discussed above. Considering that the solvent effect on coordination to metal ions is indistinct, no attempt was made to interpret these thermodynamic parameters. However, the molar ratios abstracted from ITC experiments could represent the stoichiometries of the complexes in solution.

Table 1. Thermodynamic parameters for ligands $1\!-\!3$ binding to AgBF_4 at 298 K.

	<i>n</i> ^[a]	$\beta^{[19]}$	$\frac{\Delta H^0}{[\text{kJ}\text{mol}^{-1}]}$	$\frac{T\Delta S^0}{[\text{kJ}\text{mol}^{-1}]}$
1a	0.34 ± 0.001	1.1×10^{3}	n.d. ^[b]	n.d.
2a	0.70 ± 0.04	$(1.56 \pm 0.26) \times 10^{6}$	-36.34 ± 0.44	-1.02
3	0.83 ± 0.001	$(2.90 \pm 0.18) \times 10^{6}$	-88.39 ± 0.28	-51.53

[a] *n* (molar ratio = [Metal]/[Ligand]) ratio at which an inflection point was observed on the titration curve. [b] n.d.: not determined. In the ITC experiment of **1a**, we could not obtained a complete titration curve that contained two plateaus as **2a** and **3**, because of the relatively low binding equilibrium constant β , therefore, the corresponding ΔH^0 and $T\Delta S^0$ could not be obtained precisely.

Conclusions

We have successfully designed and prepared a series of Ag^I-directed monodentate triple-stranded helicates consisting of *p*-phenylene ethynylpyridine ligands that possess Ag^I coordination sites at each pyridine unit. The X-ray single-crystal studies unambiguously established the triplestranded helical structure of [1b₃Ag]BF₄ and [2b₃Ag₂]-(BF₄)₂ in the solid state. ¹H NMR spectroscopic analysis confirmed the complexes of strands 1a, 2a, and 3 with Ag^I binding in solution. HRMS (ESI) and ITC studies showed that the stoichiometries of the triple helix formation were $1a/Ag^{I} = 3:1$, $2a/Ag^{I} = 3:2$, and $3/Ag^{I} = 1:1$, which are significantly different from the previous report that the pyridine-containing ligands and AgI ions formed doublestranded helicates.^[15] Further investigations to establish whether the ligands can coordinate other transition metal cations, especially copper(I) and palladium(II), are in progress in our laboratory.

Experimental Section

General Methods: All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. Compound **4** was synthesized according to the previously reported methods.^[21] All of the Sonogashira coupling reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents. Generally, three vacuum/purge cycles were applied to the reaction tube to remove air and refilled with nitrogen. Tetrahydrofuran (THF) and diisopropylamine (*i*Pr₂NH) were freshly distilled before use from sodium/benzophenone and CaH₂, respectively.

Single-crystal X-ray data for the helicate were collected with a Rigaku ST Saturn724+ diffractometer. NMR spectra were recorded with a 400 MHz (100 MHz for ¹³C) Bruker AV, a 500 MHz (125 MHz for ¹³C) Bruker AV III, or a 600 MHz Bruker AV spectrometer at 25 °C using residual protonated solvent signals as internal standard {¹H: δ (CDCl₃) = 7.26 ppm, δ ([D₆]acetone) = 2.05 ppm, and ¹³C: δ (CDCl₃) = 77.16 ppm}. Mass spectrometry was performed with a Shimadzu LC-MS (ESI-MS) or a Bruker-Autoflex III (MALDI-TOF MS). The metal ion complexes were measured with a Bruker-Apex IVFTMS (ESI-HRMS) and a Bruker-Solar 1X (ESI-HRMS). ITC experiments were conducted with a TAM2277–201 microcalorimetric system (Thermometric AB, Järfälla, Sweden). Melting points were measured with a Tech x-4 micro melting point apparatus.

Synthetic Procedures for Compounds 1-14

Bis{4-[(trimethylsily])ethynyl]phenyl}methane (5): To a mixture of 4 (2.24 g, 5.3 mmol), Pd(PPh₃)₄ (0.051 g, 0.27 mmol), CuI (0.312 g, 0.27 mmol), and diisopropylamine (2 mL) in THF (20 mL) was added trimethylsilylacetylene (TMSA; 1.3 g, 13.25 mmol). The reaction mixture was stirred for 12 h at room temperature then the resulting mixture was filtered. The filtrate was poured into aqueous NH₄Cl, and extracted with dichloromethane. The extract was washed with brine, dried with MgSO₄, and filtered. The filtrate was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 30:1) to give **5** (1.58 g, 83%) as a white solid.^[22]

Bis(4-ethynylphenyl)methane (6): Compound **5** (1.26 g, 3.5 mmol) was dissolved in dichloromethane (100 mL), and tetrabutylammonium fluoride (TBAF; 2.65 g, 8.4 mmol) was added. The resulting mixture was stirred at room temperature for 0.5 h then poured into water. After extraction with dichloromethane, the organic layer was washed with brine, dried with MgSO₄, and filtered. The solvent was evaporated and the residue was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 25:1) to give **6** (0.72 g, 95% yield) as a pale-yellow solid.^[22]

2,6-Bis[(trimethylsilyl)ethynyl]pyridine (7): Prepared as reported in the literature with modifications.^[23] To a mixture of 2,6-dibromopyridine (2.37 g, 10 mmol), Pd(PPh₃)₄ (0.58 g, 0.5 mmol), CuI (0.095 g, 0.5 mmol), and diisopropylamine (5 mL) in THF (20 mL), was added TMSA (2.5 g, 25 mmol). The reaction mixture was stirred for 12 h at room temperature and the resulting mixture was filtered. The filtrate was poured into aqueous NH₄Cl and extracted with dichloromethane. The organic layer was then washed with brine, dried with MgSO₄, and filtered. The filtrate was evaporated in vacuo and the residue was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 85:15) to give 7 (2.4 g, 90% yield) as a white solid.

2,6-Diethynylpyridine (8): To a solution of 7 (2.4 g, 9 mmol) in dichloromethane (100 mL) was added TBAF (6.82 g, 21.6 mmol). The resulting mixture was stirred at room temperature for 0.5 h then poured into water. After extraction with dichloromethane, the organic layer was washed with brine, dried with MgSO₄ and filtered. The solvent was evaporated and the residue was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 50:50) to give **8** (1.05 g, 92% yield) as a white solid.^[23]



2-Bromo-6-ethynylpyridine (10): Prepared as reported in the literature with modifications.^[15] To a mixture of 2,6-dibromopyridine (11.86 g, 50.1 mmol), Pd(PPh₃)₄ (0.58 g, 0.5 mmol), CuI (0.1 g, 0.5 mmol), and diisopropylamine (10 mL) in THF (40 mL), was added TMSA (0.98 g, 10.02 mmol) in THF (100 mL) dropwise over 5 h. The reaction mixture was stirred overnight at room temperature, then the resulting mixture was filtered. The filtrate was poured into aqueous NH₄Cl, and extracted with dichloromethane. The organic layer was then washed with brine, dried with MgSO₄ and filtered through a thin pad of silica gel. The filtrate was evaporated in vacuo to give a mixture of 2,6-dibromopyridine, 9, and a small amount of 7. To the residue was added dichloromethane (200 mL) and TBAF (23.8 g, 75 mmol) and the resulting mixture was stirred at room temperature for 0.5 h, and poured into water. After extraction with dichloromethane, the organic layer was washed with brine, dried with MgSO₄ and filtered. The solvent was evaporated, and the residue was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 70:30) to give recovered 2,6-dibromopyridine and 10 (1.59 g, 88% yield) as a white solid.

2-Bromo-6-[(4-butylphenyl)ethynyl]pyridine (11a): To a mixture of 1-butyl-4-iodobenzene (1.88 g, 7.2 mmol), Pd(PPh₃)₄ (0.347 g, 0.3 mmol), CuI (0.057 g, 0.3 mmol), and diisopropylamine (5 mL) in THF (20 mL) was added a solution of 10 (1.1 g, 6 mmol) in THF (10 mL). The reaction mixture was stirred overnight at room temperature, and the resulting mixture was filtered. The filtrate was poured into aqueous NH₄Cl, and extracted with dichloromethane. The organic layer was washed with brine, dried with MgSO₄, and filtered. The filtrate was evaporated in vacuo and the residue was purified by silica gel (neutral) column chromatography (hexane/ CH₂Cl₂, 80:20) to give **11a** (1.6 g, 86% yield) as a white solid, m.p. 73–75 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.56–7.40 (m, 5 H), 7.18 (d, J = 8.0 Hz, 2 H), 2.63 (t, J = 7.7 Hz, 2 H), 1.60 (dt, J =15.3, 7.5 Hz, 2 H), 1.36 (dq, J = 14.8, 7.4 Hz, 2 H), 0.93 (t, J =7.3 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 144.49$, 143.90, 141.53, 138.24, 131.90, 128.44, 127.02, 125.84, 118.71, 91.13, 86.98, 35.51, 33.13, 22.19, 13.82 ppm. MS (ESI): m/z calcd. for $C_{17}H_{16}BrN [M + H^+] 314.05$; found 314.0.

2-Bromo-6-(phenylethynyl)pyridine (11b): The synthetic procedure for **11a** was generally followed to synthesize **11b**, in which reaction the reagent 1-butyl-4-iodobenzene was substituted by iodobenzene. The reaction mixture was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 90:10) to give **11b** (0.6 g, 84% yield) as a white solid, m.p. 80–82 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (t, J = 7.8 Hz, 1 H), 7.59 (d, J = 7.7 Hz, 1 H), 7.53 (d, J = 7.7 Hz, 1 H), 7.46 (ddd, J = 13.8, 7.6, 1.0 Hz, 2 H), 7.41–7.34 (m, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 143.99, 141.84, 138.42, 132.19, 129.42, 128.52, 127.46, 126.12, 121.83, 90.91, 87.54 ppm. MS (ESI): *m/z* calcd. for C₁₃H₈BrN [M + H⁺] 257.98; found 257.9.

2-[(4-Butylphenyl)ethynyl]-6-[(trimethylsilyl)ethynyl]pyridine (12): To a mixture of **11a** (0.81 g, 2.6 mmol), Pd(PPh₃)₄ (0.15 g, 0.13 mmol), CuI (0.025 g, 0.13 mmol), and diisopropylamine (5 mL) in THF (20 mL) was added TMSA (0.31 g, 3.12 mmol). The reaction mixture was stirred for 12 h at room temperature, and the resulting mixture was filtered. The filtrate was poured into aqueous NH₄Cl and extracted with dichloromethane. The organic layer was washed with brine, dried with MgSO₄, and filtered. The filtrate was evaporated in vacuo and the residue was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 85:15) to give **12** (0.7 g, 82% yield) as a white solid, m.p. 92–94 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.62 (t, *J* = 7.8 Hz, 1 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.44 (d, *J* = 7.7 Hz, 1 H), 7.39 (d, *J* = 7.7 Hz, 1 H), 7.17 (d, J = 8.0 Hz, 2 H), 2.62 (t, J = 7.7 Hz, 2 H), 1.61 (dt, J = 15.5, 7.6 Hz, 2 H), 1.35 (dq, J = 14.7, 7.3 Hz, 2 H), 0.93 (t, J = 7.3 Hz, 3 H), 0.27 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 144.43$, 144.04, 143.46, 136.35, 132.11, 128.59, 126.52, 126.27, 119.32, 103.35, 95.36, 90.13, 87.88, 35.73, 33.38, 22.38, 13.99, -0.22 ppm. MS (ESI): m/z calcd. for C₂₂H₂₅NSi [M + H⁺] 332.18; found 332.2.

2-[(4-Butylphenyl)ethynyl]-6-ethynylpyridine (13): Compound 12 (0.7 g, 2.1 mmol) was dissolved in dichloromethane (100 mL), and TBAF (0.8 g, 2.52 mmol) was added. The resulting mixture was stirred for 0.5 h at room temperature then poured into water. After extraction with dichloromethane, the organic layer was washed with brine, dried with MgSO4 and filtered. The solvent was evaporated, and the residue was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 40:60) to give 13 (0.48 g, 89%yield) as a pale-yellow solid, m.p. 59-61 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.65 (t, J = 7.8 Hz, 1 H), 7.50 (d, J = 7.8 Hz, 2 H), 7.48 (d, J = 7.7 Hz, 1 H), 7.41 (d, J = 7.7 Hz, 1 H), 7.17 (d, J =8.0 Hz, 2 H), 3.16 (s, 1 H), 2.62 (t, J = 7.7 Hz, 2 H), 1.60 (dt, J =15.3, 7.5 Hz, 2 H), 1.35 (dq, J = 14.6, 7.2 Hz, 2 H), 0.93 (t, J =7.3 Hz, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 144.59, 144.29, 142.80, 136.53, 132.20, 128.67, 126.93, 126.34, 119.31, 90.36, 87.77, 82.52, 77.65, 35.80, 33.44, 22.45, 14.04 ppm. MS (ESI): m/z calcd. for C₁₉H₁₇N [M + H⁺] 260.14; found 260.1.

2,6-Bis{[4-(4-iodobenzyl)phenyl]ethynyl}pyridine (14): To a mixture of Pd(PPh₃)₄ (0.24 g, 0.2 mmol), CuI (0.04 g, 0.2 mmol), diisopropylamine (10 mL), THF (20 mL), and an excess of 4 (4.2 g, 10 mmol), was added a solution of 8 (0.26 g, 2 mmol) in THF (100 mL) dropwise over 6 h. The reaction mixture was stirred and heated overnight at 60 °C. After cooling to room temperature, the resulting mixture was poured into aqueous NH₄Cl, and extracted with dichloromethane. The organic layer was then washed with brine, dried with MgSO₄ and filtered. The filtrate was evaporated in vacuo and the residue was purified by silica gel (neutral) column chromatography (hexane/CH_2Cl_2, 55:45) to give 14~(1.02~g,~72%yield) as a pale-yellow solid, m.p. 217-219 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.66 (t, J = 8.0 Hz, 1 H), 7.62 (d, J = 8.2 Hz, 4 H), 7.52 (d, J = 8.1 Hz, 4 H), 7.45 (d, J = 7.8 Hz, 2 H), 7.15 (d, J =7.9 Hz, 4 H), 6.93 (d, J = 8.0 Hz, 4 H), 3.93 (s, 4 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 143.99, 141.84, 140.15, 137.79, 136.52, 132.50, 131.17, 129.09, 126.28, 120.26, 91.71, 89.88, 88.34, 41.49 ppm. MS (MALDI-TOF): m/z calcd. for $C_{35}H_{23}I_2N$ [M + H⁺] 711.99; found 712.1.

Monomer 1a: To a mixture of 1-butyl-4-iodobenzene (1.25 g, 4.8 mmol), Pd(PPh₃)₄ (0.116 g, 0.1 mmol), CuI (0.02 g, 0.1 mmol), and diisopropylamine (2 mL) in THF (20 mL) was added a solution of 8 (0.25 g, 2 mmol) in THF (10 mL). The reaction mixture was stirred overnight at room temperature then the resulting mixture was filtered. The filtrate was poured into aqueous NH₄Cl, and extracted with dichloromethane. The organic layer was washed with brine, dried with MgSO₄, and filtered. The filtrate was evaporated in vacuo, and the residue was purified by silica gel (neutral) column chromatography (hexane/CH_2Cl_2, 75:25) to give $1a~(0.7~g,~90\,\%$ yield) as a white solid, m.p. 143–145 °C. $^1\mathrm{H}$ NMR (400 MHz, CDCl₃): δ = 7.66 (t, J = 7.8 Hz, 1 H), 7.51 (d, J = 8.1 Hz, 4 H), 7.45 (d, J = 7.8 Hz, 2 H), 7.17 (d, J = 8.1 Hz, 4 H), 2.63 (t, J =7.7 Hz, 4 H), 1.60 (dt, J = 15.4, 7.6 Hz, 4 H), 1.36 (dq, J = 14.7, 7.3 Hz, 4 H), 0.93 (t, J = 7.3 Hz, 6 H) ppm. ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 144.40, 144.06, 136.39, 132.12, 128.59, 126.06, 119.37,$ 90.06, 87.98, 35.74, 33.38, 22.39, 13.99 ppm. MS (ESI): m/z calcd. for $C_{29}H_{29}N [M + H^+]$ 392.23; found 392.3.

Monomer 1b: The synthetic procedure for 1a was generally followed to synthesize 1b, in which reaction the reagent 1-butyl-4-iodo-



benzene was substituted by iodobenzene. The reaction mixture was purified by silica gel (neutral) column chromatography (hexane/ CH₂Cl₂, 80:20) to give **1b** (0.5 g, 81% yield) as a white solid, m.p. 137–139 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.69 (t, *J* = 7.8 Hz, 1 H), 7.61 (dd, *J* = 6.5, 3.2 Hz, 4 H), 7.48 (d, *J* = 7.8 Hz, 2 H), 7.41–7.34 (m, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 143.94, 136.53, 132.21, 129.19, 128.50, 126.33, 122.24, 89.76, 88.42 ppm. MS (ESI): *m/z* calcd. for C₂₁H₁₃N [M + H⁺] 280.10; found 280.1.

Dimer 2a: To a mixture of 11a (0.75 g, 2.4 mmol), Pd(PPh₃)₄ (0.06 g, 0.05 mmol), CuI (0.01 g, 0.05 mmol), and diisopropylamine (2 mL) in THF (20 mL) was added a solution of 6 (0.22 g, 1 mmol) in THF (10 mL). The reaction mixture was stirred overnight at room temperature, and the resulting mixture was filtered. The filtrate was poured into aqueous NH₄Cl, and extracted with dichloromethane. The organic layer was washed with brine, dried with MgSO₄, and filtered. The filtrate was evaporated in vacuo, and the residue was purified by silica gel (neutral) column chromatography (hexane/CH₂Cl₂, 30:70) to give 2a (0.54 g, 80% yield) as a white solid, m.p. 264–266 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (t, J = 7.8 Hz, 2 H), 7.53 (dd, J = 12.0, 8.1 Hz, 8 H), 7.45 (d, J =7.8 Hz, 4 H), 7.18 (dd, J = 8.1, 3.6 Hz, 8 H), 4.02 (s, 2 H), 2.63 (t, J = 7.7 Hz, 4 H),1.60 (dt, J = 15.3, 7.5 Hz, 4 H), 1.36 (dq, J =14.7, 7.3 Hz, 4 H), 0.93 (t, J = 7.3 Hz, 6 H) ppm. ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 144.50, 144.18, 143.99, 141.77, 136.47,$ 132.50, 132.19, 129.20, 128.66, 126.23, 126.17, 120.32, 119.40, 90.19, 89.71, 88.42, 87.98, 41.96, 35.80, 33.45, 22.45, 14.05 ppm. MS (MALDI-TOF): m/z calcd. for $C_{51}H_{42}N_2$ [M + H⁺] 683.33; found 683.6.

Dimer 2b: The synthetic procedure used for **2a** was generally followed to synthesize **2b**, in which reaction the reagent **11a** was substituted by **11b**. The reaction mixture was purified by silica gel (neutral) column chromatography (hexane/CHCl₃, 40:60) to give **2b** (0.52 g, 91% yield) as a white solid, m.p. 247–249 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (t, *J* = 7.8 Hz, 2 H), 7.61 (dd, *J* = 6.5, 3.1 Hz, 4 H), 7.54 (d, *J* = 8.1 Hz, 4 H), 7.47 (d, *J* = 8.1 Hz, 4 H), 7.42–7.32 (m, 6 H), 7.19 (d, *J* = 8.1 Hz, 4 H), 4.02 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 144.06, 143.98, 141.79, 136.51, 132.50, 132.25, 129.20, 128.52, 126.34, 126.28, 122.31, 120.29, 89.80, 89.77, 88.48, 88.38, 77.36, 41.96 ppm. MS (MALDI-TOF): *m*/*z* calcd. for C₄₃H₂₆N₂ [M + H⁺] 571.21; found 571.1.

Trimer 3: To a mixture of 14 (0.36 g, 0.5 mmol), Pd(PPh₃)₄ (0.12 g, 0.1 mmol), CuI (0.02 g, 0.1 mmol), and diisopropylamine (5 mL) in THF (20 mL) was added a solution of 13 (0.39 g, 1.5 mmol) in THF (10 mL). The reaction mixture was stirred and heated for 12 h at 60 °C. After cooling to room temperature, the resulting mixture was poured into aqueous NH₄Cl, and extracted with dichloromethane. The organic layer was washed with brine, dried with MgSO₄ and filtered. The filtrate was evaporated in vacuo, and the residue was purified by silica gel (neutral) column chromatography (hexane/CHCl₃, 10:90). The final product 3 was isolated as a white solid (0.29 g, 59% yield) by washing with CH_2Cl_2 to remove unreacted starting materials and soluble impurities, m.p. > 300 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.64 (t, J = 7.8 Hz, 3 H), 7.54 (d, J = 8.0 Hz, 8 H), 7.51 (d, J = 8.0 Hz, 4 H), 7.45–7.43 (m, 6 H), 7.19– 7.16 (m, 12 H), 4.02 (s, 4 H), 2.63 (t, J = 7.7 Hz, 4 H), 1.62 (dt, J = 15.2, 7.6 Hz, 4 H), 1.37 (dq, J = 14.6, 7.3 Hz, 4 H), 0.94 (t, J = 7.3 Hz, 6 H) ppm. ¹³C NMR (125 MHz, CDCl₃, 318 K): δ = 144.52, 144.36, 144.20, 144.16, 141.83, 141.80, 136.40, 132.56, 132.25, 129.23, 128.68, 126.27, 126.22, 126.16, 120.50, 120.47, 119.57, 90.27, 89.84, 89.78, 88.55, 88.51, 88.09, 42.04, 35.83, 33.43, 22.47, 14.00 ppm. MS (MALDI-TOF): m/z calcd. for $C_{73}H_{55}N_3$ [M + H⁺] 974.44; found 974.4.

Single Crystals for X-ray Diffraction

[1b₃Ag]BF₄: AgBF₄ (5.0 mg, 0.026 mmol) and **1b** (19.56 mg, 0.07 mmol) were dissolved in ethanol/H₂O (5 mL, 9:1, v/v) and stirred for 2 h at 50 °C. The resultant colorless solution was allowed to evaporate in the dark at room temperature for 3 weeks to give colorless polyhedrons of the Ag^I complex of **1b**.

 $[2b_3Ag_2](BF_4)_2$: To a solution of 2b (17.1 mg, 0.03 mmol) in CHCl₃ (5 mL) was added a solution of AgBF₄ (4.28 mg, 0.022 mmol) in ethanol (2 mL). After stirring for 2 h at 50 °C, a clear colorless solution was obtained. Colorless block-like crystals of the Ag^I complex of 2b were obtained by slow evaporation in darkness at room temperature for 4 weeks.

¹H MNR Titration Experiments of Ligands 1a, 2a, and 3: Ligands were dissolved in different solvents due to their distinct solubility [1a in [D₆]acetone; 2a in CDCl₃/[D₆]acetone (3:2, v/v); 3 in CDCl₃/[D₆]acetone (9:1, v/v)]. The stock AgBF₄ solutions (50.0 mM) were prepared accordingly in [D₆]acetone, CDCl₃/[D₆]acetone (3:2, v/v) and CDCl₃/[D₆]acetone (9:1, v/v), respectively, which were titrated into the solution of ligands (2.0 mM) in each portion of 2 μ L (0.1 equiv.) using a microsyringe (25 μ L). The ¹H MNR spectra was measured to observe the change 10 min after injection of AgBF₄ solution. The titration was finished when no further significant change was observed.

HRMS (ESI) of Ag^I Complexes of 1a and 2a

Ag^I Complex of 1a: $AgBF_4$ (11.68 mg, 0.06 mmol) and 1a (11.74 mg, 0.03 mmol) were dissolved in acetone (5 mL) and stirred for 2 h at 50 °C. After cooling to room temperature, the clear colorless solution was obtained for HRMS (ESI) measurement.

Ag^I Complex of 2a: To the solution of 2a (13.65 mg, 0.02 mmol) in CHCl₃ (2 mL) was added a solution of AgBF₄ (7.79 mg, 0.04 mmol) in acetone (5 mL), and the mixture was stirred for 2 h at 50 °C. The solvent was evaporated, and the resulting residue was dissolved in acetone (5 mL) for HRMS (ESI) measurement.

Isothermal Titration Microcalorimetry (ITC): The calorimetric measurements were made by using a stainless steel sample cell (1 mL) at 25.00 ± 0.01 °C. The sample cell of the microcalorimeter was initially loaded with 600 µL solvent or ligand solution [2.0 mM of 1a in ethanol; 1.0 mM of 2a in CHCl₃/ethanol (3:2, v/v); 1.0 mM of 3 in CHCl₃/ethanol (9:1, v/v)]. Concentrated metal solution [8.5 mM in ethanol, 2.5 mM in CHCl₃/ethanol (3:2, v/v), 2.5 mM in CHCl₃/ethanol (9:1, v/v) for the corresponding titration of 1a, 2a and 3] was injected consecutively into the stirred sample cell in portions of 5, 10, and 5 µL, respectively, using a 500 µL Hamilton syringe controlled by a Thermometric 612 Lund pump until the desired concentration range had been covered. During the whole titration process, the system was stirred at 60 rpm with a gold propeller, and the interval between two injections was sufficiently long for the signal to return to the baseline. The enthalpy (ΔH^0) was obtained by integrating the areas of the peaks in the plot of thermal power against time. The reproducibility of experiments was within ±4%.

CCDC-974845 (for $[1b_3Ag]BF_4$) and -974846 (for $[2b_3Ag_2](BF_4)_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Supporting Information (see footnote on the first page of this article): 1D-NOEDIF spectra, 2D NMR spectra, ¹H NMR titration experiments, HRMS (ESI), ITC measurements, crystal structure determination, ¹H and ¹³C NMR spectra.



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