

7-Azaindoly- and 2,2'-Dipyridylamino-Functionalized Molecular Stars with Sixfold Symmetry: Self-Assembly, Luminescence, and Coordination Compounds

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Abstract: Two novel star molecules functionalized with 7-azaindoly and 2,2'-dipyridylamino groups have been synthesized. Both molecules possess a sixfold rotation symmetry. Molecule **L1** is based on the hexaphenylbenzene core with the formula of hexa[*p*-(7-azaindoly)phenyl]benzene, while molecule **L2** is based on the hexakis(biphenyl)benzene core with the formula of hexa[*p*-(2,2'-dipyridylamino)biphenyl]benzene. Both compounds have been characterized by single-crystal X-ray diffraction analyses. Molecule **L1** forms extended two-dimensional layered structure, while **L2** forms interpenetrating columnar stacks in the solid state, as revealed by X-ray diffraction analyses. Nanowire structures

based on columnar stacks through self-assembly of **L2** on a graphite surface were revealed by an STM study. Molecules **L1** and **L2** are capable of binding to metal ions, resulting in unusual structural motifs. Two Ag^I complexes with the formulae of [(AgNO₃)₂(**L1**)] (**1**) and [(AgNO₃)₃(**L1**)] (**2**) were isolated from the reactions of AgNO₃ with **L1**. Compound **1** displays extended intermolecular π - π stacking interactions that are responsible for its extended two-dimensional structure in

the crystal lattice. Complex **2** has a "bowl" shape and forms polar stacks in the crystal lattice. A Cu^{II} complex with the formula of [[Cu(NO₃)₂]₆(**L2**)] (**3**) was isolated from the reaction of Cu(NO₃)₂ with compound **L2**. The six Cu^{II} ions in **3** are chelated by the 2,2'-dipyridylamino groups of the star ligand **L2**. Intermolecular Cu-O (nitrate) bonds lead to the formation of an extended two-dimensional coordination network of **3**. Both **L1** and **L2** are blue luminescent. Their interactions with Ag^I or Cu^{II} cause drastic quenching of emission. In addition, the luminescence of **L1** and **L2** is sensitive to the presence of protons, which cause a reduction of emission intensity and a red shift of the emission energy.

Keywords: luminescence • molecular stars • self-assembly • structure elucidation • supramolecular chemistry

Introduction

Highly branched molecules or molecules that have a star shape (or starburst) are an important class of molecules for materials scientists owing to some of their very attractive features. It has been demonstrated by several research groups^[1] that starburst molecules often perform better than nonstarburst molecules in organic light emitting diodes (OLEDs), either as charge-transport materials or as emit-

ters, owing to their tendency to form stable amorphous films with a relatively high T_g . Furthermore, starburst molecules make it possible to incorporate multiple charge-transfer (or redox) sites in a single molecule, thus facilitating their use as charge-transport materials in organic devices.^[2a-c] It has been envisioned that starburst molecules functionalized by donor atoms can be used for binding to multiple catalytically active metal centers, thus enhancing the overall catalytic activity and perhaps, more importantly, introducing new capability to the catalyst that is not possible to achieve in a mononuclear metal complex.^[2d-h] In addition, starburst molecules with Lewis base sites have been shown to be effective building blocks for the assembly of unusual extended supramolecular structures through either hydrogen bonds or coordination bonds.^[3] In contrast to starburst molecules with threefold symmetry^[1,3a,4] (e.g., trisubstituted benzene, trisubstituted 1,3,5-triazine or triarylamine), which are becoming

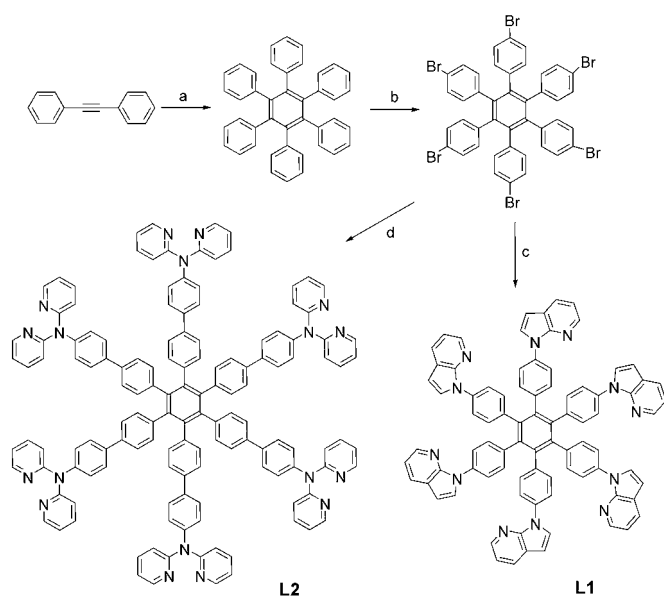
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abundant in literature, examples of functionalized starburst molecules with sixfold symmetry that are emissive and capable of binding to metal ions remain scarce. Our group has recently reported a series of highly luminescent trisubstituted benzene and triazine molecules with 7-azaindolyl or 2,2'-dipyridylamino functionality and their uses in OLEDs and luminescent supramolecular assembly.^[3a,4] We have now extended our investigation to hexasubstituted benzene molecules. The behavior of the hexasubstituted benzene molecules is very different from that of trisubstituted ones in term of extended structures, self-assembly, and supramolecular network formation with metal ions. Herein we report two new hexasubstituted benzene molecules that contain either 7-azaindolyl functional groups or 2,2'-dipyridylamino functional groups, their structural and luminescent properties, their interactions with Lewis acids such as metal ions and protons, and their uses in self-assembly and the formation of supramolecular structures.

Results and Discussion

Syntheses of star molecules **L1 and **L2**:** The molecular stars **L1** and **L2** were synthesized by using the procedure shown in Scheme 1. The key starting material, hexakis(4-bromo-



Scheme 1. Reagents and conditions: a) $[\text{PdCl}_2(\text{PhCN})_2]$ acetone; b) Br_2 , CH_2Cl_2 ; c) 7-azaindole, CuI , K_3PO_4 , *trans*-diaminocyclohexane, 110°C ; d) *p*-(2-py) $_2\text{PhB}(\text{OH})_2$, Na_2CO_3 , $[\text{Pd}(\text{PPh}_3)_4]$, toluene, ethanol, H_2O , reflux.

phenyl)benzene, was synthesized by using a modified literature procedure.^[5] The Ullmann condensation^[6] reaction of hexakis(4-bromophenyl)benzene with 7-azaindole with K_3PO_4 and CuI (as a base and a catalyst, respectively) produced compound **L1** in moderate yield (40%). Pd-catalyzed Suzuki–Miyaura cross-coupling^[7] of hexakis(4-bromophe-

nyl)benzene with *p*-(2,2'-dipyridylamino)phenyl boronic acid^[8] afforded compound **L2** in good yield (61%). Compound **L1** is fairly soluble in most common polar solvents such as THF, CH_2Cl_2 , and CH_3COOEt . Compound **L2** has a poor solubility in THF, CH_2Cl_2 , or CH_3COOEt , but is moderately soluble in chloroform. Both compounds display a very high melting point (316°C for **L1**, 358°C for **L2**). Compounds **L1** and **L2** display oxidation peaks at 1.44 and 1.20 V (versus AgCl/Ag), respectively, in the cyclic voltammetry diagrams recorded in CH_2Cl_2 . Both compounds were fully characterized by NMR spectroscopy, and elemental and single-crystal X-ray diffraction analysis. NMR spectra of **L1** and **L2** established that the six legs in these two molecules are equivalent in solution.

Crystal structures of **L1 and **L2**:** The crystal structure of **L1** is shown in Figure 1. The six 7-azaindolylphenyl legs in **L1** are all perpendicular to the central benzene ring to minimize steric interactions. In the crystal lattice, molecules of **L1** form extended two-dimensional layered structures. Within each layer, the molecules of **L1** interdigitate through the six legs with weak interleg π – π interactions, as depicted in Figure 1 (middle). These layers are all oriented in the same direction, but do not form columnar stack. Instead the layers alternate in an ABAB fashion with the neighboring layers off-setting each other, and between the layers there is little interaction other than van der Waals forces.

The molecule of **L2** has a crystallographically imposed inversion center as shown in Figure 2. All 2,2'-dipyridylamino units in **L2** are disordered (see Supporting Information), which along with many not fully resolved solvent molecules in the lattice contribute to the poor quality of the crystal data. Nevertheless, the X-ray data revealed some distinct features for **L2**. The diameter of molecule **L2** is ~ 3 nm. It is a flat molecule with the thickness varying from 0.35–0.45 nm. In contrast to the extended two-dimensional layered structure of **L1**, molecules of **L2** form extended columnar stacks (Figure 2 middle and bottom). These stacks interpenetrate through the legs. There is, however, no significant π – π interaction between the legs. The disordering of the dipyridyl units on the periphery of the molecule is clearly caused by the large size of the molecule and the lack of strong intermolecular π stacking interactions in the crystal lattice.

Self-assembly of molecular star **L2** on a graphite surface:

The crystal structures of **L1** and **L2** demonstrated that such molecular stars are capable of self-assembling into a highly ordered structure in the solid state. To determine if the same is true on surfaces, we examined the behavior of molecule **L2** on a graphite surface by using STM imaging methods. After a diluted solution of **L2** in CHCl_3 was placed on the surface of a highly oriented pyrolytic graphite (HOPG), the resulting graphite surface was examined by STM, which revealed the presence of many wirelike structures on surface. The width of these wires ranges from 14 nm to 26 nm (the height of the wires cannot be accurately measured.).

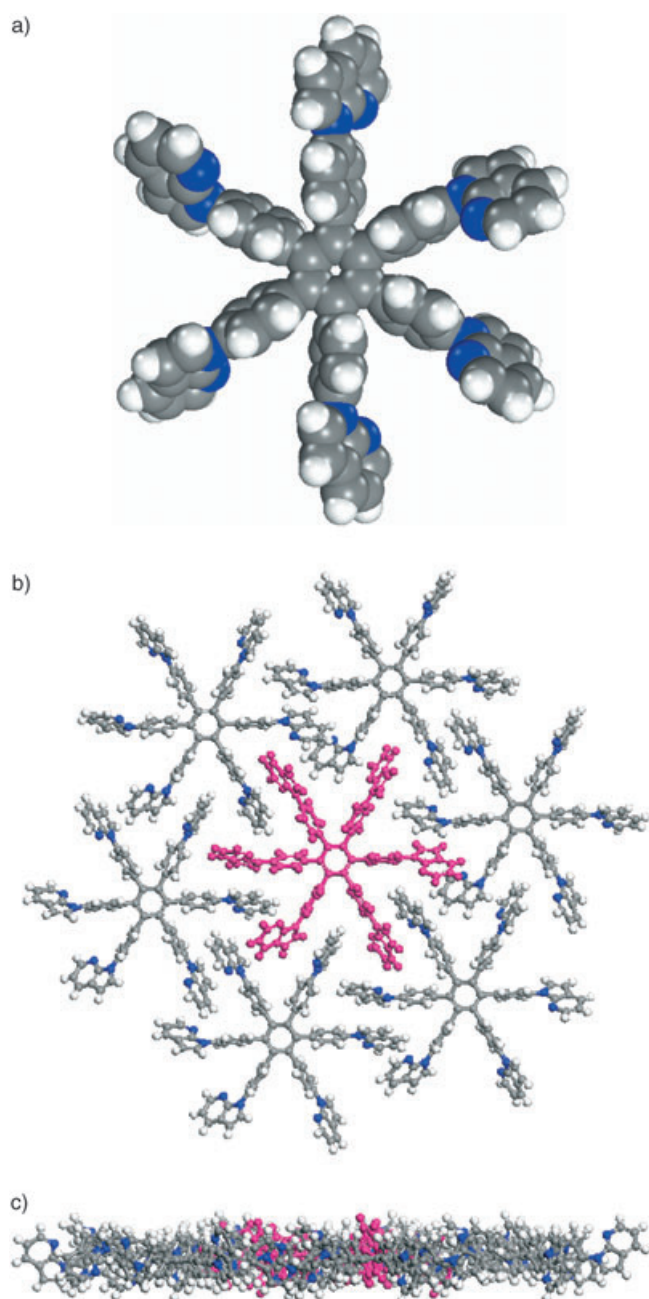


Figure 1. Top: The molecular structure of **L1** shown as space-filling diagram (blue: nitrogen). Middle: A diagram showing the intermolecular interaction within a single layer. Bottom: Side view of the same layer depicted in the middle.

An STM image of a wire is shown in Figure 3. This image bears striking resemblance to the columnar stacks of **L2** in the crystal lattice as revealed by X-ray diffraction. We therefore believe that these wires are probably a consequence of self-assembly by molecules of **L2** that form stacks with the molecular plane being perpendicular to the graphite surface. This behavior is not surprising, considering the fact that the six biphenyl legs in **L2** are all perpendicular to the molecular plane, hence there is little advantage for the molecules

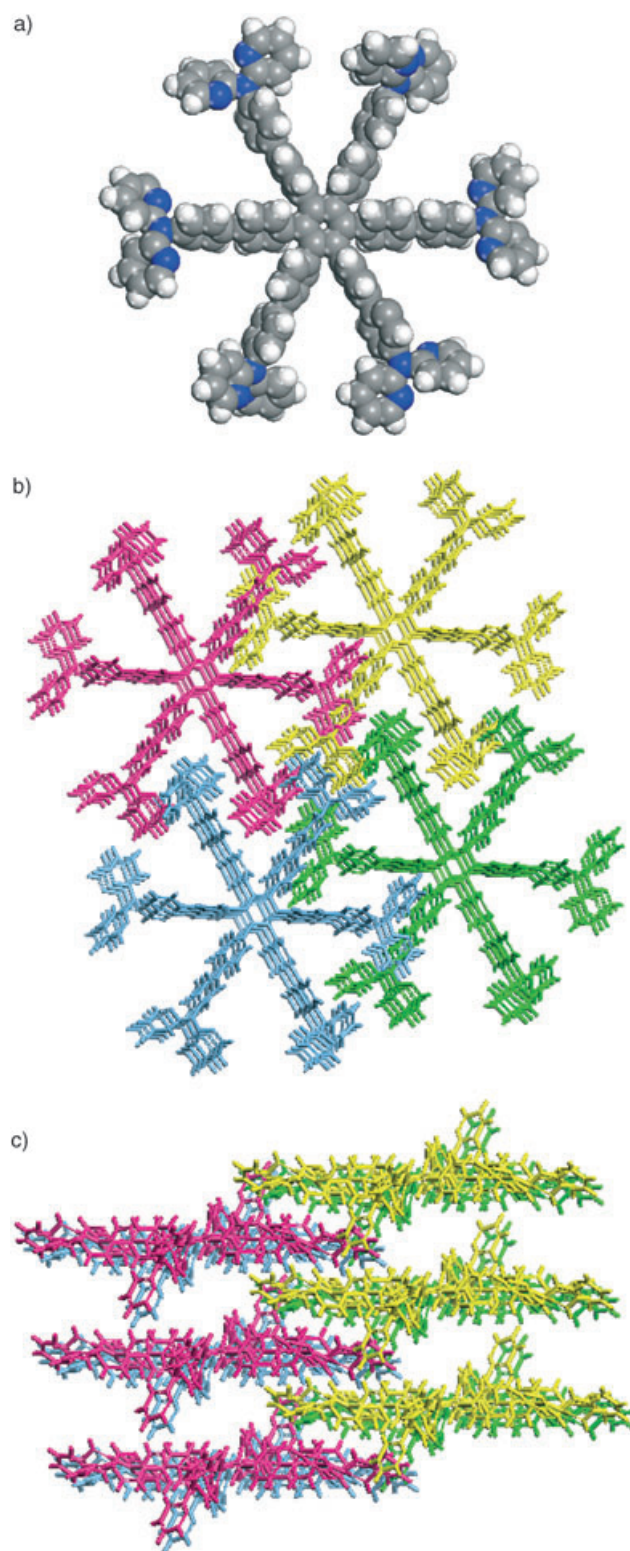


Figure 2. Top: The molecular structure of **L2** shown as a space-filling diagram (blue: nitrogen). Middle: A diagram showing the inter-penetrated columns. Bottom: Side view of the same columns depicted in the middle.

to stack with the molecular plane parallel to the graphite surface. Taking into consideration of interpenetration of the columns shown in Figure 2 (middle and bottom), the ob-

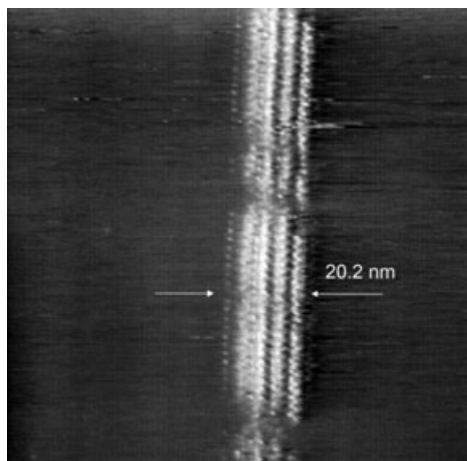


Figure 3. An STM image of a self-assembled wire of **L2** on a graphite surface (width = 20.2 ± 0.6 nm).

served widths of the wires correspond to ~ 6 – 14 molecules. The STM images established that molecules of **L2** can indeed self-assemble into ordered, nanoscale structures on surfaces.

Coordination compounds of **L1 and **L2**:** To establish the utility of **L1** and **L2** as building blocks for the formation of extended structures through coordination bonds, we examined the reactions of **L1** and **L2** with three representative metal ions Ag^{I} , Zn^{II} , and Cu^{II} in various ratios. For ligand **L1**, complex **1** with the formula of $[(\text{AgNO}_3)_2(\text{L1})]$ was isolated from the reaction of **L1** with AgNO_3 in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ with either a 1:1 or a 1:2 ratio of the ligand and AgNO_3 in the reaction. When the reaction of **L1** with AgNO_3 was carried out in a 1:6 ratio, complex **2** with the formula of $[(\text{AgNO}_3)_3(\text{L1})]$ was obtained in good yield. Complex **2** can also be obtained by using a 1:3 ratio of **L1** versus AgNO_3 . Complex **1** is only slightly soluble in CHCl_3 , while **2** only shows appreciable solubility in methanol. For ligand **L2**, complex **3** with the formula of $[(\text{Cu}(\text{NO}_3)_2)_6(\text{L2})] \cdot x\text{H}_2\text{O}$ was isolated in good yield from the reaction of **L2** with $\text{Cu}(\text{NO}_3)_2$ in a 1:6 ratio by using a $\text{CH}_3\text{CN}/\text{THF}/\text{CHCl}_3$ solvent-layering technique. Complex **3** exists in at least two crystalline forms—small blue-green needles and dark green hollow needles with thin walls. The difference between these two forms appears to be the number of H_2O ligands associated with the Cu^{II} centers, based on CHN analysis. Complex **3** is insoluble in most organic solvents except DMF and DMSO. No Zn^{II} complexes were isolated from the reactions of ZnCl_2 or $\text{Zn}(\text{O}_2\text{CCF}_3)_2$ with **L1** or **L2**.

Crystal structures of complexes: Crystals of **1** and **2** suitable for X-ray diffraction analyses were obtained and both structures were determined successfully by single-crystal X-ray diffraction analysis. For complex **3**, the dark green crystals were capable of producing weak diffraction and were therefore used for X-ray diffraction. However, the data obtained are very poor.

The molecular structure of complex **1** is shown in Figure 4. Two Ag^{I} ions are coordinated to the star ligand **L1** and are related to each other by an inversion center. Each Ag^{I} ion is bound by two 7-azaindolyl groups through the nitrogen atoms. The third position is occupied by the nitrate

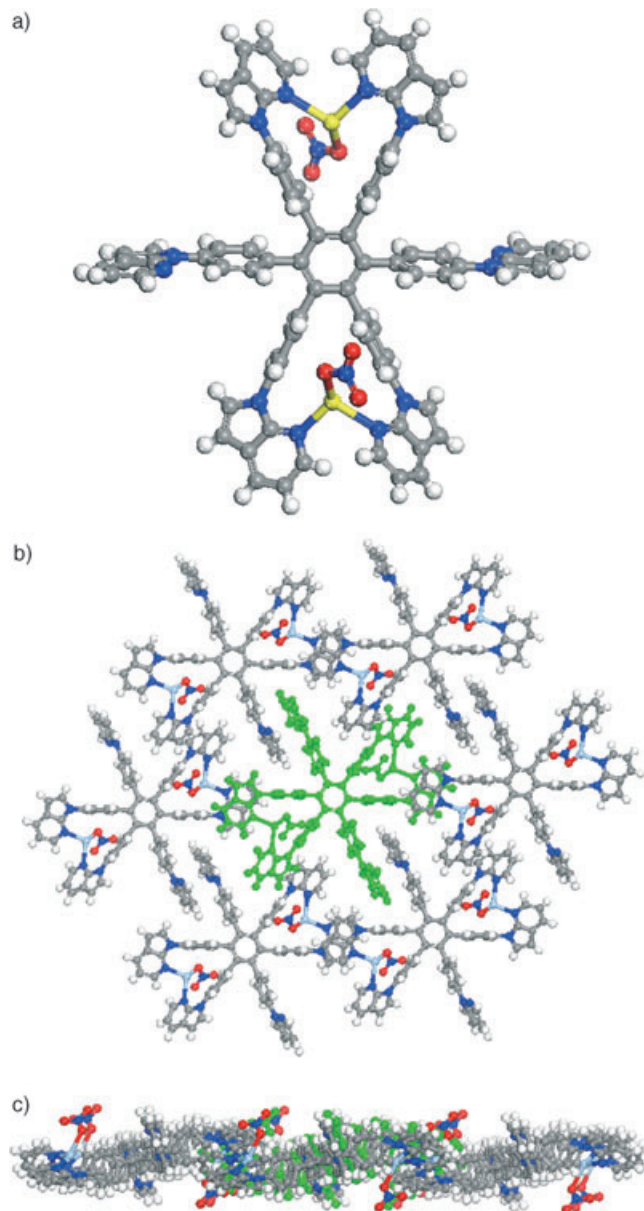


Figure 4. Top: The molecular structure of **1** shown as a stick and ball diagram (blue: nitrogen; red: oxygen; yellow: silver). Middle: A diagram showing the intermolecular interaction within a single layer. Bottom: Side view of the same layer depicted in the middle.

anion as a terminal ligand. The remaining oxygen atoms of the nitrate are more than $3 \text{ \AA}$ away from the Ag^{I} center. The geometry around the Ag^{I} is approximately trigonal planar. The most striking feature of **1** is the intermolecular interaction present in the crystal lattice. Molecules of **1** form extended two-dimensional layers through π – π stacking

between the 7-azaindolyl rings of adjacent molecules. As shown in Figure 4 (middle), each of the six legs of molecule **1** is paired up with a leg from the neighboring molecule with the atomic separation distances between the two 7-azaindolyl rings ranging from 3.6–4.0 Å. In other words, each molecule of **1** is locked into position by pairing up with six neighboring molecules in the crystal lattice. Unlike the free ligand, the two-dimensional layers of **1** stack in the lattice. The binding of the Ag^I ion to the ligand clearly causes a change in the extended structure. In solution, complex **1** displays a highly dynamic behavior. The ¹H NMR spectrum of **1** in CD₂Cl₂ at ambient temperature shows one set of broad chemical shifts for the protons on the 7-azaindolylphenyl leg, which are resolved into two distinct sets of chemical shifts with ~1:1 ratio at low temperature (Figure 5), an indication that compound **1** undergoes a dynamic exchange in

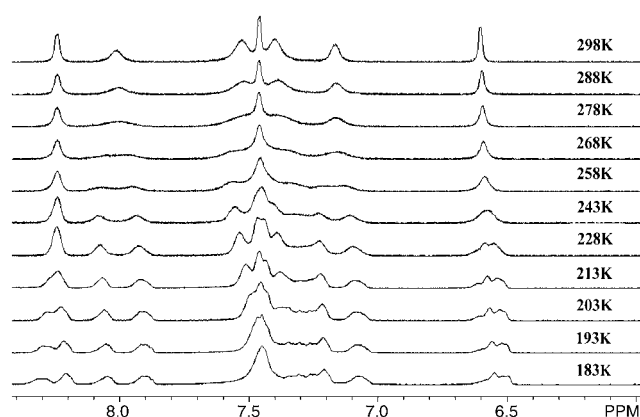


Figure 5. Variable-temperature ¹H NMR spectra of **1** in CD₂Cl₂.

solution. This exchange is likely an intramolecular process, that is, involving the migration of the Ag^I ions among the six 7-azaindolyl binding sites, based on the behavior of complex **2** (see discussion below). However, since the two sets of chemical shifts are not 1:2 ratio, the structure of **2** in solution at low temperature (183 K) is probably not the same as the crystal structure.

The molecular structure of **2** is shown in Figure 6. Compound **2** possesses crystallographically imposed C₃ symmetry. Each Ag^I ion is bound by two 7-azaindolyl groups in a manner similar to that in **1**. One notable difference is that the second oxygen atom of the nitrate ligand is weakly bound to the Ag^I ion in **2** (Ag...O = 2.66(1), 2.599(9) Å for the two independent molecules). In addition, in contrast to **1**, in which the two AgNO₃ units are on the opposite sides of the molecular plane, the three AgNO₃ units in **2** are all on the same side. As a consequence, complex **2** has a “bowl” shape. The “bowls” are all oriented along the same direction in the crystal lattice of **2**, perhaps driven by the electrostatic interactions between the electronegative nitrate and the electropositive protons on **L1**. As a consequence, the crystals of **2** belong to the polar space group R3. There

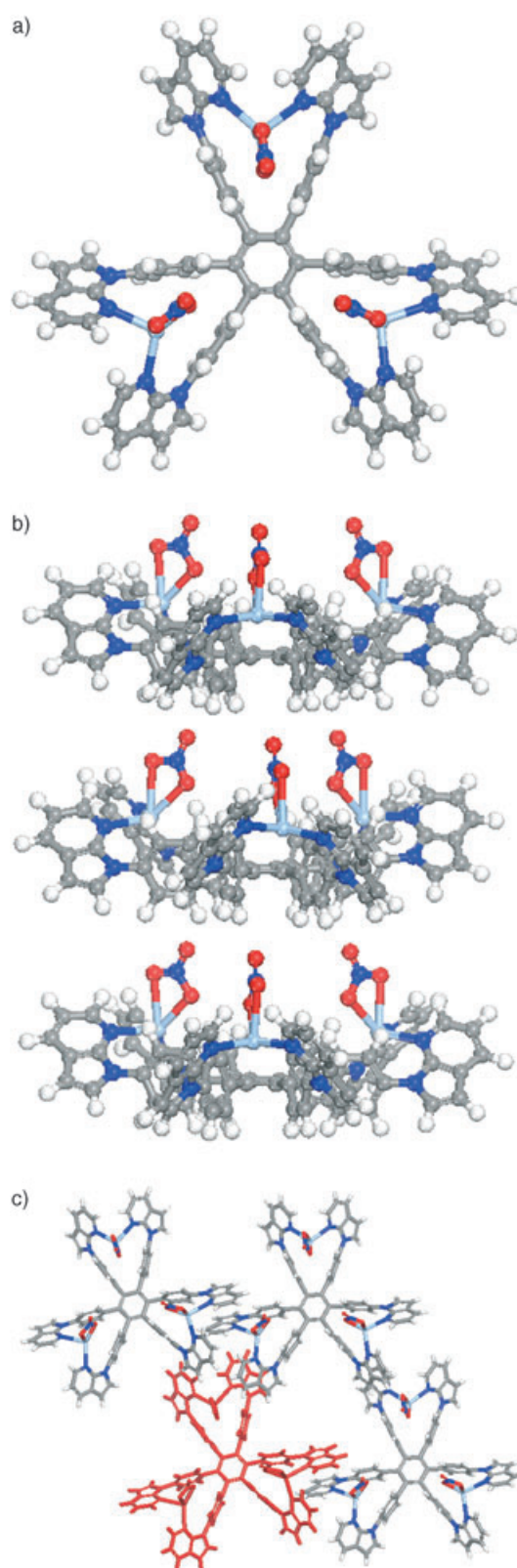


Figure 6. Top: The molecular structure of **2** shown as a stick and ball diagram (blue: nitrogen; red: oxygen; light blue: silver). Middle: A diagram showing the orientation of three AgNO₃ units and the stacking of **2**. Bottom: A diagram showing the intermolecular interactions within a single layer.

are weak intermolecular π - π interactions among the 7-azaindolyl groups in the crystal of **2**, as shown by Figure 6, but not all 7-azaindolyl legs are paired up with legs from neighboring molecules. The shortest atomic separation distance between two neighboring 7-azaindolyl rings is 4.0 Å. In contrast to the behavior of **1**, compound **2** does not display any dynamic exchange in solution, as evidenced by its ^1H NMR spectrum. The lack of dynamic exchange of **2** can be explained by the fact that all the 7-azaindolyl binding sites in **2** are occupied by the Ag^{I} ions; hence there are no vacant sites available for Ag^{I} ions to undergo intramolecular migration. The absence of dynamic exchange of **2** also lead us to conclude that the exchange phenomena displayed by **1** must be caused by the vacant 7-azaindolyl binding sites in **1**, hence most likely an intramolecular exchange process. Dynamic exchanges involving metal ions and vacant binding sites on starburst molecules have been observed previously.^[4b]

The molecular structure of complex **3** is shown in Figure 7. Due to the weak diffraction, the twinning of the crystal, the disordering of the $\text{Cu}(\text{NO}_3)_2$ and pyridyl units, and the unresolved large number of solvent molecules in the crystal lattice, the structural data is poor, despite our repeated efforts (four data sets from four different crystals were collected for **3** at 120 K, which all showed consistently the same structural features.). The bond lengths and angles for **3** are not accurate. However, we have confidence in the basic structural features revealed by the X-ray data. The molecule of **3** possesses a crystallographically imposed inversion center. There are six Cu^{II} ions chelated to the six 2,2'-dipyridylamino groups in **3**. Each Cu^{II} ion is also bound by two intramolecular nitrate ligands. Two of the Cu^{II} ions ($\text{Cu}(1)$, $\text{Cu}(1\text{A})$) are bound by a H_2O ligand. Most interestingly, the $\text{Cu}(1)$ and $\text{Cu}(1\text{A})$ centers are linked to $\text{Cu}(3')$ and $\text{Cu}(3\text{A}')$ from neighboring molecules through a nitrate bridge ($\text{Cu}(3')\text{--O}(2) \approx 2.48$ Å). As a result, the $\text{Cu}(1)$ and $\text{Cu}(3)$ centers can be best described as five-coordinate. Due to the disordering of the nitrate ligands (and the pyridyl rings which cannot be modeled), there are some uncertainties on the bonding modes of some of the intramolecular nitrate ligands (i.e., terminal versus chelating). There are no intermolecular coordination bonds between the $\text{Cu}(2)$ and $\text{Cu}(2')$ centers. Nevertheless, as a consequence of the nitrate bridges between

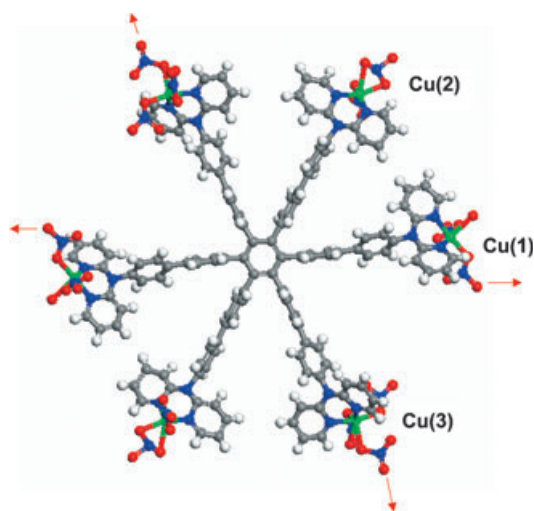


Figure 7. The molecular structure of **3** shown as a stick and ball diagram (blue: nitrogen; red: oxygen; green: copper). The direction of intermolecular Cu-O bonds is indicated by arrows.

$\text{Cu}(1)$ and $\text{Cu}(3')$, molecules of **3** form an extended two-dimensional network, as shown in Figure 8. This two-dimensional network is in sharp contrast with the one-dimensional columnar stack of the free ligand **L2**. In addition, the two-dimensional network of **3** forms ladderlike stacks with adjacent layers. The structure of **3** demonstrates again that coordination bonds can be used to modulate the extended structure of large molecular star molecules such as **L2**.

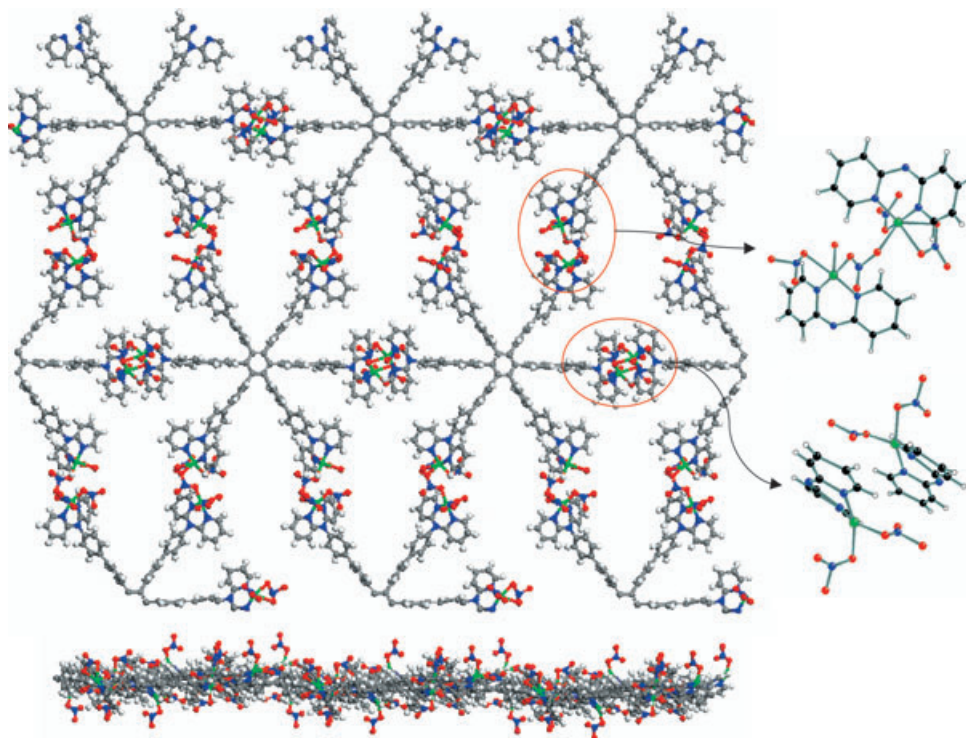


Figure 8. Top: A diagram showing the Cu-O bond linked two-dimensional network of **3**. Bottom: Side view of the same layer.

Luminescence: Molecules **L1** and **L2** are luminescent in solution and the solid state with the emission maximum in the violet (~380 nm) and blue (~400 nm) regions, respectively. Compared to 4,4'-bis(7-azaindolyl)-1,1'-biphenyl ($\lambda_{\text{max}} = 405$ nm), the emission band of **L1** is significantly blue-shifted, which can be attributed to the lack of conjugation of the 7-azaindolylphenyl leg with the central benzene ring in **L1**, imposed by steric interactions. The emission band of **L2** is, however, similar to that of 4,4'-bis(2,2'-dipyridylamino)-1,1'-biphenyl ($\lambda_{\text{max}} = 401$ nm); this is not surprising, since the 2,2'-dipyridylamino biphenyl leg in **L2** has a similar conjugation length as 4,4'-bis(2,2'-dipyridylamino)-1,1'-biphenyl. However, the emission quantum yields (~24 %) for **L1** and **L2** are considerably lower than that of the corresponding disubstituted biphenyl compound (> 50 %); this difference is very likely caused by the close proximity of the six legs in **L1** and **L2**, hence significant interleg quenching of luminescence. The luminescent data are listed in Table 1.

Table 1. Luminescent data of compounds **L1**, **L2**, **1**, and **2**

	Emission (excitation) in CH ₂ Cl ₂ , λ_{max} [nm]	Emission (excitation) solid, λ_{max} [nm]
L1	379 (307)	380 (358)
L2	401 (360)	409 (372)
1	380 (315)	428 (371)
2	376 (328) (CH ₃ OH)	392 (328)

Effect of metal ions on luminescence of **L1 and **L2**:** The formation of metal complexes such as **1–3** causes a drastic change in the luminescence. The Ag^I complexes **1** and **2** display a blue emission in solution with λ_{max} similar to that of the free ligand **L1**. Both complexes are also luminescent in the solid state with a distinct difference. For **1** the solid emission maximum is at 438 nm, considerably red-shifted, relative to that found in solution. For **2**, the solid emission maximum is at 392 nm, also red-shifted, but much less than that found for **1**, relative to the solution emission spectrum (in CH₃OH). The red shift of the emission bands of **1** and **2** in the solid state is most likely caused by intermolecular π – π interactions between the 7-azaindolyl portions of the molecule; such interactions are known to shift the emission energy to a longer wavelength.^[9] The different extent of red shift displayed by **1** and **2** is clearly associated with the different extent of π – π interactions present in the crystal lattices of **1** and **2**, as revealed by the crystal structures. Because **1** has much more intense and more extensive intermolecular π – π stacking interactions than **2** does in the solid state, complex **1** shows a greater emission red shift than **2**. To quantify the effect of Ag^I ions on the emission of ligand **L1**, we recorded the emission band change in the presence of Ag^I ions. As shown in Figure 9, the addition of one equivalent of AgNO₃ (in CH₃CN) to the solution of **L1** (8.12×10^{-5} M) in CH₂Cl₂ resulted in the decrease of emission intensity by ~55 %. The addition of two equivalents of AgNO₃ resulted in the reduction of emission intensity to ~4 % of the initial intensity. Further addition of AgNO₃ did not lead to further

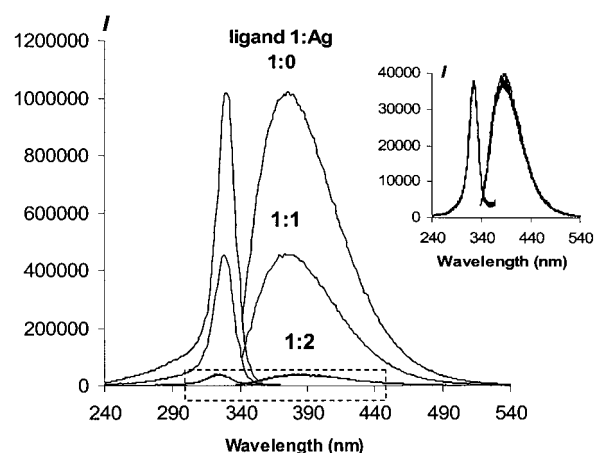


Figure 9. Excitation and emission spectra of **L1** (8.12×10^{-5} M in CH₂Cl₂) with various ratios of **L1** versus AgNO₃.

decrease of emission intensity. The coordination of Ag^I ions to ligand **L1** as demonstrated by the structures of **1** and **2** is clearly responsible for the observed luminescence quenching.

The paramagnetic Cu^{II} ions completely quench the emission of the ligand **L2**, as demonstrated by the absence of luminescence of **3**. To determine the amount of Cu^{II} ions required to cause complete quenching of luminescence from **L2**, we did a titration experiment; the results are shown in Figure 10. The addition of one equivalent of Cu^{II} ions

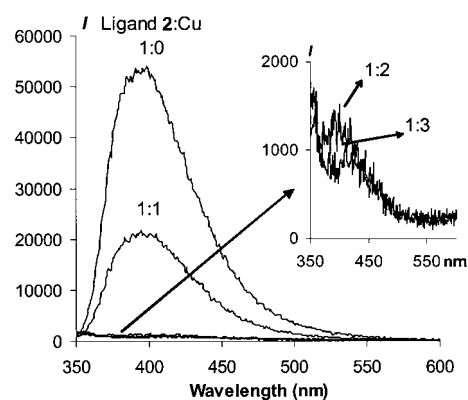


Figure 10. Excitation and emission spectra of **L2** (5.0×10^{-6} M in CHCl₃) with various ratios of **L2** versus Cu(NO₃)₂.

(Cu(NO₃)₂ in THF) to the solution of **L2** (5.0×10^{-6} M) in CHCl₃ causes a decrease of emission intensity ~60 %. The addition of two equivalents of Cu^{II} ions essentially completely quenches the emission of the ligand. The binding of Cu^{II} ions to the dipyridylamino units in **L2** brings the paramagnetic Cu^{II} center close to the chromophore, which is clearly responsible for the observed luminescence quenching.

Effect of protons on luminescence of **L1 and **L2**:** Protons are attracted to the lone pair electrons of the nitrogen

atoms in **L1** and **L2** just as the metal ions are. Therefore, one would anticipate that protons are also likely to exert some effects on the emission of **L1** and **L2**. Indeed, both compounds were found to have a very sensitive response to the presence of protons. For **L1**, as shown by Figure 11, the

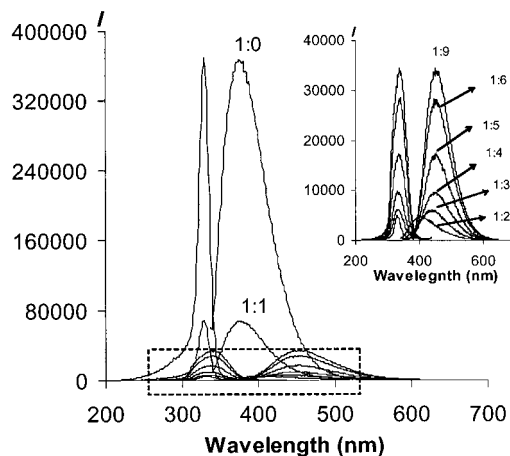


Figure 11. Excitation and emission spectra of **L1** (8.12×10^{-5} M in CH_2Cl_2) with various ratios of **L1** versus $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$.

addition of one equivalent of protons ($[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$, $\text{Ar}' = 3,5\text{-bis(trifluoromethyl)phenyl}$) to the solution of **L1** (8.12×10^{-5} M) in CHCl_3 resulted in $\sim 82\%$ reduction of the emission intensity without significantly shifting the emission energy. The addition of two equivalents of protons to the solution of **L1** caused a decrease of emission intensity by $\sim 98\%$ and the shift of the emission band from $\lambda_{\text{max}} = 379$ to ~ 400 nm. Interestingly, however, further addition of protons resulted in a gradual shift of the emission band to $\lambda_{\text{max}} = 460$ nm and a steady increase of emission intensity, which reaches the maximum ($\sim 10\%$ of the initial emission intensity) at the 1:9 ratio of **L1** versus protons. Further increase of the proton concentration does not change the spectrum further. The emission color of the solution of **L1** changed visibly from dark blue to sky blue after the addition of three equivalents of protons. Clearly the overall effect of the addition of protons is luminescent quenching. The partial recovery of the emission intensity after the addition of more than three equivalents of protons is likely due to the formation of proton chelating between two pyridyl groups; this may enhance the rigidity of the molecule, and, hence, the emission intensity.

The addition of one equivalent of protons ($[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$) to the solution of **L2** (2.50×10^{-6} M) in CHCl_3 caused about 62% decrease of emission intensity without change of emission energy (Figure 12). The addition of two equivalents of protons resulted in a decrease of $\sim 90\%$ emission intensity. Addition of five or more equivalents of protons caused the emission maximum to shift from 400 to 422 nm with very weak emission intensity ($\sim 2\%$ of initial intensity). The red shift of emission peak is similar to the behavior of **L1**. However, in contrast to the behavior of **L1**, no

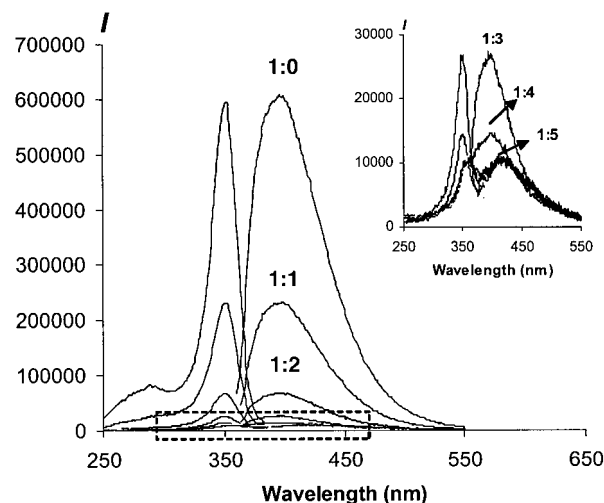


Figure 12. Excitation and emission spectra of **L2** (2.50×10^{-6} M in CHCl_3) with various ratios of **L2** versus $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$.

recovery of emission intensity was observed at a higher ratio of protons versus **L2** ($> 6:1$). Luminescence quenching by protons by means of acid–base interactions has been well documented previously.^[9] Protonated forms of **L1** and **L2** are most likely responsible for the observed luminescence quenching.

Conclusion

We have demonstrated that 7-azaindolyl- and 2,2-dipyridyl-amino-functionalized star molecules based on the hexaphenylbenzene core can be synthesized in good yield by either Ullmann condensation or Suzuki coupling methods. These molecules form layered or columnar structures in the solid state. The large star molecule **L2** is capable of self-assembling into nanowire structures on surfaces. The 7-azaindolyl and 2,2'-dipyridylamino Lewis base sites in the star molecules **L1** and **L2** make it possible to assemble them together through metal–ligand bonds, as demonstrated by the two-dimensional extended structure of complex **3**. In addition, the binding of metal ions such as Ag^{I} to the star molecule such as **L1** considerably alters the extended arrangement of the star molecules in the solid state. Based on the results of our preliminary study, the new functionalized star molecules are very promising in forming various organized structures in the solid state and on surfaces. The binding of metal ions to the star molecules causes a drastic quenching of luminescence from star ligands. When Ag^{I} ion is used, the resulting complexes are still luminescent, but with a much lower intensity relative to that of the free ligand. In contrast, paramagnetic metal ions such as Cu^{II} can lead to a complete quenching of the luminescence. Such a luminescent response toward metal ions by the functionalized star molecules may be useful for selective and sensitive detection of various metal ions. The luminescent quenching phenomena displayed by protons resemble that of the Ag^{I} ions. However,

unlike Ag^+ ions, which only cause the decrease of emission intensity, protons cause both emission intensity decrease and the shift of emission energy, depending on the concentration of protons. Therefore, the new star molecules also have the potential as a pH probe. Systematic and quantitative examination on this aspect of application is underway in our laboratory.

Note Added in Proof

Since this manuscript was submitted for publication we have taken some very high-resolution images of molecular wires on graphite. These images clearly show both the corrugation produced by beta-site carbon atoms and the internal structure of the wires. Concurrently, we found in the published work of C. R. Clemmer and T. P. Beebe^[10] an image collected from a cleaved graphite surface that contains a wire-like feature that the authors associated with a step edge. Although we have been able to induce large surface-defect densities of the familiar moiré type^[11] by exposing graphite to solvents, we have not yet observed wirelike features on graphite without adsorbing molecules. However, we are now extending our experiments to other surfaces to exclude the possibility that in some or all cases the wirelike features arise from defects in the underlying graphite and not from the molecular compound. These experiments will be described in a future publication.

Experimental Section

All starting materials were purchased from Aldrich Chemical Company and used without further purification. Solvents were freshly distilled over appropriate drying reagents. All experiments were carried out under a dry nitrogen atmosphere by using standard Schlenk Techniques unless otherwise stated. TLC was carried out on SiO_2 (silica gel F254, Whatman). Flash chromatography was carried out on silica (silica gel 60, 70–230 mesh). ^1H and ^{13}C spectra were recorded on Bruker Avance 300, 500 MHz spectrometers. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model 2 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia (Canada). Melting points were determined on a Fisher–Johns melting point apparatus. *p*-(2,2'-Dipyridylamino)bromobenzene, *p*-(2,2'-dipyridylamino)phenylboronic acid,^[8] and hexaphenylbenzene^[12] were synthesized by using modified literature methods.

Preparation of hexakis(4-bromophenyl)benzene: Br_2 (2 mL) was slowly added to a solution of hexaphenylbenzene (1.2 g) in CH_2Cl_2 (10 mL). The mixture was stirred overnight, then saturated Na_2SO_3 aqueous solution (30 mL) was added slowly with stirring. The aqueous phase was extracted with CH_2Cl_2 (3×15 mL). The product (2.25 g) was obtained after the solvent was removed by vacuum in 99% yield, and was used without further purification. ^1H NMR (CDCl_3 , 25°C): δ = 7.08 (d, J = 8.4 Hz, 12H), 6.63 ppm (d, J = 8.4 Hz, 12H).

Preparation of hexakis[*p*-(7-azaindoly)phenyl]benzene (L1): A mixture of hexakis(4-bromophenyl)benzene (0.80 g, 0.79 mmol), 7-azaindole (0.60 g, 5.0 mmol), CuI (0.051 g), K_3PO_4 (2.12 g), *trans*-1,2-diaminocyclohexane (0.37 mL), and 1,4-dioxane (8 mL) was stirred at 110°C for 48 h. After workup, colorless crystals of the product were obtained in 40% yield (0.40 g). ^1H NMR (CDCl_3 , 25°C): δ = 8.27 (dd, J = 4.8, 1.5 Hz, 6H; 7-azain), 7.85 (dd, J = 7.8, 1.5 Hz, 6H; 7-azain), 7.53 (d, J = 8.7 Hz, 12H; Ph), 7.44 (d, J = 3.6 Hz, 6H; 7-azain), 7.15 (d, J = 8.7 Hz, 12H; Ph), 7.03

(dd, J = 7.8, 4.8 Hz, 6H; 7-azain), 6.48 ppm (d, J = 3.6 Hz, 6H; 7-azain); ^{13}C NMR (CDCl_3 , 25°C): δ = 147.95, 143.82, 141.09, 138.55, 136.99, 133.09, 129.40, 128.28, 122.49, 122.10, 117.09, 102.12 ppm; elemental analysis calcd (%) for $\text{C}_{84}\text{H}_{54}\text{N}_{12}$: C 81.95, H 4.39, 13.66; found: C 81.48, H 4.52, N 13.34; m.p. 316°C.

Preparation of hexakis[*p*-(2,2'-dipyridylamino)biphenyl]benzene (L2): A mixture of hexakis(4-bromophenyl)benzene (0.50 g, 0.496 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.15 g), and toluene (40 mL) was stirred for 10 min. *p*-(2,2'-Dipyridylamino)phenylboronic acid (0.953 g, 3.27 mmol) in EtOH (20 mL) and NaOH (0.8 g) in H_2O (20 mL) were subsequently added. The mixture was stirred and refluxed for 48 h and allowed to cool to room temperature. The water layer was separated and extracted with CHCl_3 (3×30 mL). The combined organic layers were dried over MgSO_4 , and the solvents were evaporated under reduced pressure. Purification of the crude product by column chromatography (CH_2Cl_2 /Hexane/THF, 1:2:3) afforded **2** as a colorless solid in 61% yield. ^1H NMR (CDCl_3 , 25°C): δ = 8.32 (dd, J = 5.0, 1.0 Hz, 12H; Py), 7.54 (ddd, J = 8.5, 7.0, 2.0 Hz, 12H; Py), 7.50 (d, J = 8.5 Hz, 12H; Ph), 7.20 (d, J = 8.5 Hz, 12H; Ph), 7.17 (d, J = 8.5 Hz, 12H; Ph), 7.02 (d, J = 8.5 Hz, 12H; Ph), 6.98 (d, J = 8.5 Hz, 12H; Py), 6.92 ppm (dd, J = 7.0, 5.0 Hz, 12H; Py); ^{13}C NMR (CDCl_3 , 25°C): δ = 158.50, 148.90, 144.32, 140.68, 140.04, 138.28, 137.88, 137.35, 132.34, 128.39, 127.72, 125.57, 118.49, 117.41 ppm; elemental analysis calcd (%) for $\text{C}_{138}\text{H}_{96}\text{N}_{18} \cdot \text{CH}_2\text{Cl}_2$: C 79.85, H 4.69, N 12.06; found: C 80.08, H 4.74, N 11.90; m.p. 358°C.

Preparation of [(AgNO₃)₂(L1)] (1): AgNO_3 (5.6 mg, 0.033 mmol) in MeOH (2 mL) was added to a solution of **L1** (20 mg, 0.016 mmol) in a minimum amount of CH_2Cl_2 and stirred for 0.5 h. After the solution was allowed to stand for two days in the dark, colorless crystals of **1** were obtained in 45% yield. ^1H NMR (CD_2Cl_2 , 25°C): δ = 8.24 (brs, 6H; 7-azain), 8.14 (brs, 6H; 7-azain), 7.56 (brs, 12H; Ph), 7.46 (brs, 6H; 7-azain), 7.40 (brs, 12H; Ph), 7.17 (brs, 6H; 7-azain), 6.60 ppm (brs, 6H; 7-azain); elemental analysis calcd (%) for $\text{C}_{84}\text{H}_{54}\text{Ag}_2\text{N}_{14}\text{O}_6 \cdot \text{CH}_2\text{Cl}_2$: C 61.63, H 3.38, N 11.84; found: C 61.84, H 3.18, N 11.87.

Preparation of [(AgNO₃)₃(L1)] (2): AgNO_3 (17 mg, 0.098 mmol) in MeOH (2 mL) was added to a solution of **L1** (20 mg, 0.016 mmol) in a minimum amount of CH_2Cl_2 and stirred for 0.5 h. After the solution was allowed to stand for a few days in the dark, colorless crystals of **2** were obtained in 88% yield. ^1H NMR (CD_3OD , 25°C): δ = 7.66 (d, J = 7.5 Hz, 6H; 7-azain), 7.47 (d, J = 4.5 Hz, 6H; 7-azain), 7.10 (d, J = 3.5 Hz, 6H; 7-azain), 6.90 (d, J = 8.0 Hz, 12H; Ph), 6.81 (d, J = 8.0 Hz, 12H; Ph), 6.74 (dd, J = 8.0, 5.0 Hz, 6H; 7-azain), 6.60 ppm (d, J = 3.5 Hz, 6H; 7-azain); elemental analysis calcd (%) for $\text{C}_{84}\text{H}_{54}\text{Ag}_3\text{N}_{15}\text{O}_9 \cdot 2.5\text{H}_2\text{O}$: C 56.48, H 3.31, N 11.77; found: C 56.21, H 3.18, N 11.81.

Preparation of [(Cu(NO₃)₂)₆(L2)] (3): A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (14 mg, 0.06 mmol) in THF (5 mL) was added to a solution of **L2** (19 mg, 0.01 mmol) in CHCl_3 (5 mL). The mixture became cloudy. The mixture became a clear solution after addition of CH_3CN (8 mL). The solution was stirred overnight and toluene (2 mL) was added. After the solution was allowed to stand for two weeks, dark green crystals of **3** were obtained in 68% yield. Elemental analysis calcd (%) for $\text{C}_{138}\text{H}_{96}\text{Cu}_6\text{N}_{30}\text{O}_{36} \cdot 6\text{H}_2\text{O}$: C 51.16, H 3.34, N 12.97; found: C 51.39, H 3.11, N 12.31.

STM imaging: Highly oriented pyrolytic graphite (HOPG) samples (Advanced Ceramics, grade ZYH), were mounted on glass slides by using conductive epoxy (Epoxy Technologies, H21D). Surfaces with large regions of atomically flat (0001) crystal orientation were prepared by removing several graphite layers with cellophane tape. Subsequently, two drops of an approximate 0.1 mg mL^{-1} solution of **L2** in chloroform were added. STM images were acquired in air under ambient conditions by using a home-built beetle-type microscope.^[13] The images were obtained in constant-current mode by using mechanically-formed PtIr tips. Lateral calibration of the piezoelectric scanner was based on the 0.246 nm spacing of beta-site atoms on the graphite surface. Images are presented without filtering, although a background subtraction was applied.

X-ray crystallographic analysis: Single crystals of **L1** were obtained from slow diffusion of hexane into a solution of **L1** in CH_2Cl_2 . Crystals of **L2** were obtained from mixed solvents of hexane, toluene, CH_2Cl_2 , and THF. The crystals of **1** and **2** were obtained from hexane, CH_2Cl_2 , and methanol. The crystals of **3** were obtained from a mixture of solvents of tolu-

Table 2. Crystal data for compounds **L1**, **L2**, and **1–3**.

	L1	L2 ^[c]	1	2	3 ^[c]
formula	C ₈₄ H ₅₄ N ₁₂	C ₁₃₈ H ₉₆ N ₁₈ ·3 CHCl ₃ ·3 THF·3 C ₆ H ₅ CH ₃	C ₈₄ H ₅₄ Ag ₂ N ₁₄ O ₆ ·2 CH ₂ Cl ₂ ·5 CH ₃ OH	C ₈₄ H ₅₄ N ₁₅ O ₉ Ag ₃ ·2 CH ₂ Cl ₂ ·3.75 CH ₃ OH·2.5 H ₂ O·0.75 C ₆ H ₁₄	C ₁₃₈ H ₁₀₀ N ₃₀ O ₃₈ Cu ₆ ·5.5 C ₆ H ₅ CH ₃ ·x H ₂ O
<i>M_r</i>	1231.39	3618.45	1901.21	2140.8	3671.3
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>P</i> 1	<i>R</i> 3	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	17.099(5)	9.4077(19)	10.089(5)	18.233(3)	9.191(3)
<i>b</i> [Å]	12.510(4)	18.504(4)	13.841(7)	18.233(3)	29.520(12)
<i>c</i> [Å]	29.612(9)	21.967(4)	16.139(7)	18.233(3)	34.831(14)
α [°]	90	88.74(3)	105.329(8)	107.411(3)	90
β [°]	90.397(7)	80.80(3)	105.016(8)	107.411(3)	91.012(8)
γ [°]	90	82.14(3)	92.664(8)	107.411(3)	90
<i>V</i> [Å ³]	6334(3)	3739.5(13)	2083.2(17)	4990.3(14)	9449(6)
<i>Z</i>	4	1	1	2	2
ρ_{calcd} [g ^{−1} cm ^{−3}]	1.291	1.606	1.515	1.425	~1.278
μ [mm]	0.078	0.522	0.670	0.758	0.741
2 θ_{max} [°]	57.04	54.90	56.60	56.56	56.98
reflns measured	45527	35513	14219	25353	67212
reflns used (<i>R</i> _{int})	15286 (0.1204)	16373 (0.1871)	9238 (0.0321)	11514 (0.037)	21858 (0.2165)
parameters	865	930	555	794	931
<i>R</i> 1 ^[a] [<i>I</i> > 2 σ (<i>I</i>)]	0.0634	0.1744	0.1037	0.0490	0.1560
<i>wR</i> 2 ^[b] [<i>I</i> > 2 σ (<i>I</i>)]	0.1106	0.3512	0.2946	0.1172	0.3068
<i>R</i> 1 ^[a] (all data)	0.2918	0.4482	0.1462	0.0764	0.4622
<i>wR</i> 2 ^[b] (all data)	0.1500	0.4249	0.3135	0.1256	0.3748
goodness of fit on <i>F</i> ²	0.706	1.033	1.033	0.968	1.285

[a] $R1 = \sum [|F_o| - |F_c|] / \sum |F_o|$. [b] $wR2 = \{\sum [w(F_o^2 - F_c^2)] / \sum (wF_o^2)\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075 P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [c] Weakly diffracting crystals with a large number of lattice solvent molecules missing or partially located.

ene, CHCl₃, and CH₃CN. Crystals **L1**, **1**, and **2** were mounted on thin glass fibers for data collection. Crystals **L2** and **3** were sealed in glass capillaries along with solvents. Data were collected on a Siemens P4 single-crystal X-ray diffractometer with a CCD-1000 detector and graphite-monochromated Mo_{K α} radiation, operating at 50 kV and 30 mA at 293 K for **L1**, at 120 K for **L2** and **3**, at 180 K for **1** and **2**. No significant decay was observed for all samples. Data were processed on a PC using Bruker SHELXTL software package^[14] (version 5.10). Crystals of **L2**, **1**, and **3** belong to the triclinic space group *P*1. Crystals of **L1** belongs to the monoclinic crystal space group *P*2₁/*n* and crystals of **2** belong to the rhombohedral space group *R*3. All structures were solved by direct methods. All non-hydrogen atoms except those of disordered solvent molecules in **L1**, **1**, and **2** were refined anisotropically. All hydrogen atoms except those of disordered solvent molecules in **L1**, **1**, and **2** were calculated and their contributions were included in structural factor calculations. Crystals of the big star molecule **L2** and its complex **3** diffract poorly and weakly. In addition, the groups along the periphery of molecules **L2** and **3** display severe thermal disordering, perhaps due to the large size of the molecule (~3 nm in diameter). The Cu^{II} ions in **3** also display significant thermal disordering. However, due to the limited number of reflections, this disorder could not be fully addressed. Furthermore, there are a large number of solvent molecules in the crystal lattices of **L2** and **3** (3 CHCl₃, 3 THF, 3 toluene molecules per molecule of **L2** were located in the crystal lattice; 5.5 toluene and 1 H₂O molecules per molecule of **3** were found in the lattice). These solvent molecules were all disordered and were only partially resolved and refined. As a consequence of poor diffraction, disordering of the molecules, disordering of solvent molecules, and perhaps missing solvent molecules, the crystal data of **L2** and **3** are poor, despite repeated data collections and the use of different crystals. The results from our best efforts for **L2** and **3** along with crystal data for **L1**, and its complexes **1** and **2** are included in Table 2. CCDC-246905 (**L1**), CCDC-246906 (**L2**), CCDC-246902 (**1**), CCDC-246903 (**2**), and CCDC-246904 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

We thank J. M. MacLeod for generously sharing her knowledge of preparation and STM imaging of graphite. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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Received: August 5, 2004
Published online: November 25, 2004