Coordination Networks

Luminescent 2D Macrocyclic Networks Based on Starburst Molecules: $[\{Ag(CF_3SO_3)\}_{1.5}(tdapb)]$ and $[\{Ag(NO_3)\}_3(tdapb)]$**

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Luminescent supramolecular architectures have recently attracted much research interest primarily because of their potential applications in optoelectronic devices and as fluorescent sensors and probes.[1–7] One of the most effective and attractive approaches for the assembly of supramolecular architectures is the use of coordination bonds. It has been demonstrated extensively by many researchers that by choosing appropriate metal ions and organic building blocks, it is possible to control and manipulate the structures and the resultant properties (electronic, photonic, magnetic, and catalytic) of the supramolecular materials.[8–13] One way to induce large cavities in supramolecular structures based on coordination compounds is to employ a large organic linker that has well-defined shape and coordination geometry. Large starburst or star-shaped ligands are attractive candidates for this purpose because they form interesting and uncommon extended structures such as hexagonal or triangular macrocycles. Although a few triangle-shaped ligands have been reported as successful linkers for extended cyclic structures,[7,14] examples of this class of supramolecular structures remain relatively scarce.

Recently we reported a class of triangular starburst molecules that contain three 2,2′-dipyridylamino chelating sites.[15] We demonstrated that these molecules are efficient blue emitters for organic light-emitting diodes and are capable of binding to metal centers such as Zn^{II} and Pt^{II} through the pyridyl groups to form various discrete starburst metal complexes.[16] One of the metal complexes, $[(ZnCl_2)_3(tdapb)]$ (tdapb = 1,3,5-tris(4-(2,2′-dipyridylamino)-phenyl)benzene), has been shown by our group to be a highly selective and sensitive fluorescent sensor for benzene. A crystal structural study revealed that the molecular shape and the extended structure of $[(ZnCl_2)_3(tdapb)]$ in the solid state are responsible for its high affinity for benzene molecules and the consequent effective fluorescent quenching by the incorporated solvent.[17]

Encouraged by this finding and intrigued by the possibility of using the tdapb ligand as a triangular linker to achieve novel extended luminescent structures, we investigated the coordination chemistry of tdapb with Ag^I ions. Although Zn^{II} and Ag^I ions have the same electronic configurations, the Ag^I ion has a much stronger tendency to display versatile and often irregular coordination geometry than the Zn^{II} ion. As a consequence, the Ag^I ion is much more accommodating toward the ligand and is expected to form extended structures more readily than the Zn^{II} ion.

Two different Ag^I salts, $Ag(NO_3)$ and $Ag(CF_3SO_3)$ were used in our investigation. The reactions of tdapb with $Ag(CF_3SO_3)$ and with $Ag(NO_3)$ in a 1:3 ratio under the same conditions resulted in the formation and isolation of two distinct 2D coordination polymers with the formulae $[\{[Ag(CF_3SO_3)]_{1.5}(tdapb)\}_n]$ (**1**), and $[\{[Ag(NO_3)]_3(tdapb)\}_n]$ (**2**), respectively. The crystals of both compounds are solvated by benzene, methanol, and dichloromethane molecules, and lose these solvent molecules rapidly when isolated from solution. Compounds **1** and **2** are air-stable.

Crystals **1** and **2** belong to the trigonal space group $R\bar{3}$ and $R\bar{3}c$, respectively, as determined by X-ray diffraction analyses; the connectivity between the Ag^I ions and the tdapb ligands in **1** and **2** is shown. The local coordination environment around the Ag^I ions in both compounds is shown in Figure 1. In **1**, only one of the pyridyl groups from each of the 2,2′-dipyridylamino (dpa) units is coordinated to the Ag^I ion, whereas in **2** both pyridyl groups of the dpa unit are bound to Ag^I ions. In **1**, one Ag^I ion links two dpa units from two neighbouring tdapb ligands together, whereas in **2** the same

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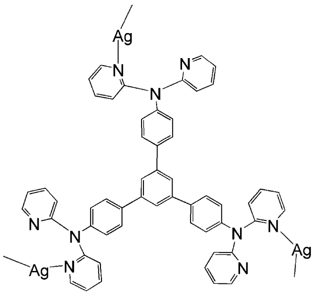
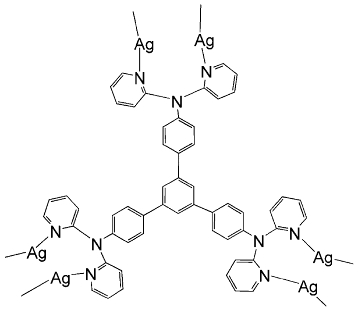


[{Ag(CF_3SO_3)}$_{1.5}$(tdapb)] (**1**)



[{Ag(NO_3)}$_3$(tdapb)] (**2**)

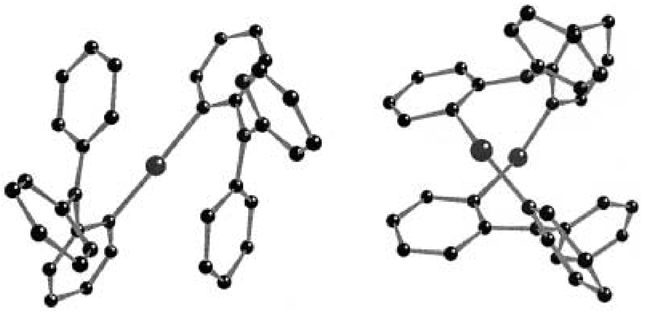


Figure 1. The coordination environment of Ag^I ions in **1** (left) and **2** (right).

linkage employs two Ag^I ions. Each Ag^I ion in **1** and **2** is bound by two nitrogen atoms with normal Ag–N bond lengths in an approximately linear fashion for **1** (N-Ag-N′ = 171.17(15)°) and in a bent manner for **2** (N-Ag-N = 141.6(5)°,143.1(4)°). The anions $CF_3SO_3^-$ in **1** and NO_3^- in **2** are weakly bound to the Ag^I ions through one oxygen atom with a long Ag–O bond (Ag–O = 2.73(2) Å for **1**, 2.56(2) Å for **2**). As a consequence, the Ag^I ion in both compounds has a distorted three-coordinate geometry.

In **1**, six tdapb ligands are linked together by six Ag^I ions in an alternating *up* and *down* fashion to form an approximately honeycomb-shaped macrocycle as shown in Figure 2. The distance between the two opposite pairs of Ag ions on the macrocycle is ~21 Å. A benzene solvent molecule is located in the center of the macrocyclic cavity, and other solvent molecules such as CH_2Cl_2 and CH_3OH are also located inside the cavity along with the anions. The macrocyclic structure of **1** propagates along two dimensions, resulting in the formation of a 2D layer (Figure 2b). These 2D layers are arranged in the crystal in an *ABAB* fashion resembling that of hexagonal close packing, such that the macrocyclic cavity does not form extended channels. Solvent molecules are found in the space between the 2D layers. Crystals of **1** with a Star-of-David shape can be sheared readily into thin triangular plates by manipulating them with a needle, which is a manifestation of the 2D layered structure.

In **2**, six tdapb ligands are linked together by twelve Ag^I ions in a similar *up* and *down* fashion to compound **1**, to form a macrocyclic structure. However, in contrast to the honeycomb structure of **1**, the macrocycle of **2** has an unusual cloverleaf shape as shown in Figure 3. As a result, the macrocyclic cavity of **2** is much smaller than that of **1** and no benzene solvent molecule is located inside the cavity; CH_3OH and CH_2Cl_2 solvent molecules along with the anions, however, are again found in the cavity as seen with **1**. There are no significant interactions between the solvent molecules and the host framework. The macrocycles of **2** propagate along two dimensions in the same manner as **1** to form a 2D macrocyclic network (Figure 3b). The 2D networks of **2** also stack in an

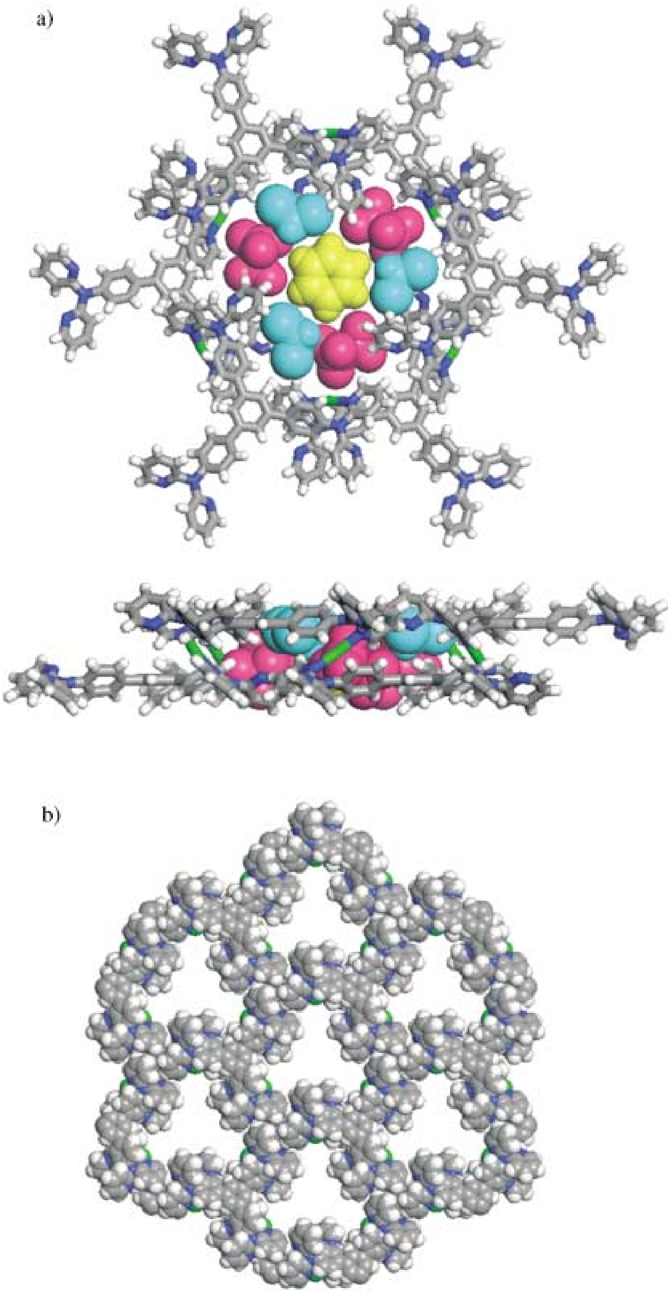


Figure 2. a) The single honeycomb-shaped cavity in **1** (top view and side view). Anions and solvent molecules are shown as space-filling models. Ag: green, N: dark blue, $CF_3SO_3^-$: purple, CH_2Cl_2: light blue, C_6H_6: yellow. Three methanol solvent molecules located above the benzene ring are omitted for clarity. b) The 2D extended framework of **1** shown as a space-filling model with anions and solvent molecules removed.

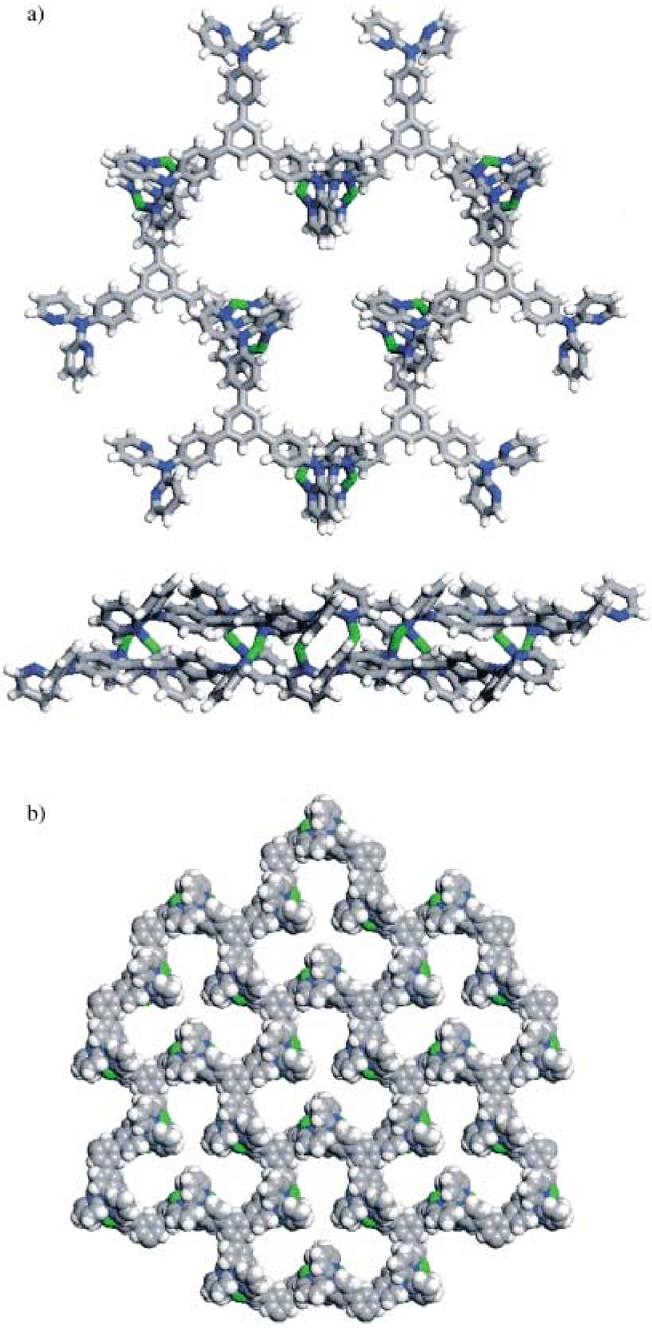


Figure 3. a) The single cloverleaf-shaped cavity in **2** (top view and side view). Anions and solvent molecules are not shown owing to disordering. Ag: green, N: dark blue. b) The 2D extended framework of **2** shown as a space-filling model with anions and solvent molecules removed.

ABAB fashion, resulting again in the absence of solvent channels perpendicular to the 2D layer.

The striking difference between the macrocyclic structure of **1** and **2** is clearly caused by the different number of Ag^I ions present in the framework. In the syntheses of **1** and **2**, the same 1:3 molar ratios of ligand to Ag was used, and yet from the reaction of $Ag(CF_3SO_3)$ with tdapb, only the 1:1.5 product **1** was isolated consistently. The anion appears to have played a key role in the formation of structures **1** and **2**. The NO_3^- anion is a stronger donor than the $CF_3SO_3^-$ anion as indicated by the relatively short Ag–O (NO_3^-) bond length and the bent N-Ag-N angle in **2**. This, along with the fact that the NO_3^- anion is much smaller than $CF_3SO_3^-$, perhaps facilitates the binding of two Ag^I ions at each connecting point between the two tdapb ligands and the formation of a relatively small cavity in **2**. Anion-dependent extended structures have been observed frequently.[18] However, the relationship between a given anion and the selective formation of a certain type of supramolecular structures is not yet well understood.

1 and **2** are insoluble in common organic solvents. They are slightly soluble in polar solvents such as DMSO, which appear to break down the extended framework and result in the formation of discrete molecular compounds, based on the similar NMR and emission spectra of **1**, **2**, and the free ligand in solution. When irradiated with UV light at ambient temperature, the free ligand tdapb displays bright blue luminescence with λ_{max} at ~400 nm in both the solution (CH_2Cl_2) and the solid states.[15] . Solid samples of **1** and **2** show no detectable luminescence at ambient temperature. However, an intense green emission (λ_{max} at 489 nm, 523 nm for **1**, λ_{max} at 489 nm, 527 nm for **2**) was observed upon excitation of both compounds at 77 K (Figure 4). The green emission of the complexes was determined to be phosphorescence, based on their microsecond-order decay lifetimes (6–10 μs). At 77 K, the free ligand tdapb also displays a very weak phosphorescent emission band in the same region as that of **1** and **2** (Figure 4). Therefore, we believe that the green emission of the complexes at 77 K originates from the tdapb ligand.

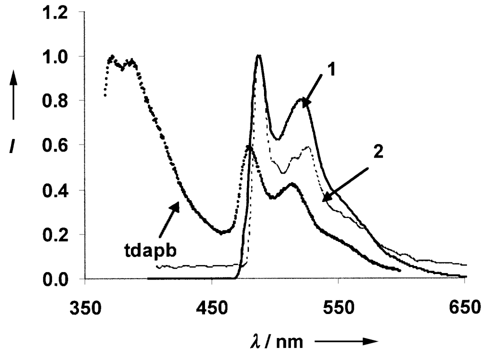


Figure 4. The emission spectra of the free ligand tdapb in CH_2Cl_2 solution at 77 K (excitation at 355 nm) and of **1** and **2** in the solid state at 77 K (excitation at 386 nm and 381 nm, respectively).

The absence of detectable fluorescence emission from the complexes in the solid state could be attributed to quenching by the Ag^I ions and interlayer π–π stacking interactions. The Ag^I ion appears to enhance the phosphorescence emission of the ligand since the green emission of the complexes is much brighter (readily visible to the naked eye) than that of the free ligand. Phosphorescence enhancement through the heavy atom effect is a well-known phenomenon,[19] and many examples have been reported previously.[20] For example, a frozen solution of the tdapb–Pt^{II} complex $[Pt_3Ph_6(tdapb)]$ in

CH_2Cl_2 displays a ligand-based blue-green phosphorescence band similar to those observed in the case of **1** and **2**.[20e]

In summary, two novel 2D networks with nanoscale cavities based on a starburst molecule and coordination bonds involving Ag^I ions have been demonstrated. The formation of these unusual structures appears to be anion-dependent. These new networks have large cavities for solvent molecules such as benzene and CH_2Cl_2. The absence of luminescence at ambient temperature precludes their use as fluorescent sensors for organic molecules based on quenching. However, they may find use as sensors/probes based on guest-induced fluorescent enhancement, which is currently being explored in our laboratory.

Experimental Section

The ligand tdapb was synthesized according to published methods.[1] All syntheses and recrystallizations were conducted in air, in a fumehood, in reaction vials covered with aluminum foil to prevent light-induced decomposition of the silver salts. Elemental analyses were performed by Canadian Microanalytical Services, Delta, BC, Canada. ^1H NMR spectra were recorded on Bruker Avance 300, or 400, or 500 MHz spectrometers. Fluorescent spectra were recorded on a Photon Technologies International Quantamaster Model C-60 spectrometer. UV/Vis absorption spectra were recorded on a HP8542A Diode Array Spectrophotometer.

1: Upon a solution of tdapb (50 mg, 0.0614 mmol) in CH_2Cl_2 (6 mL) were successively layered benzene (4 mL), methanol (4 mL), and a solution of $Ag(CF_3SO_3)$ (47 mg, 0.184 mmol) in methanol (6 mL). The vial was covered in aluminum foil, and the solvents were allowed to diffuse slowly over several days to afford colorless crystals of **1** (68 mg, 92 %). Elemental analysis: calcd for $Ag_{1.5}C_{55.5}H_{39}N_9O_{4.5}\cdot 1.5\,CH_2Cl_2$: C 52.73, H 3.17, N 9.50; found: C 51.82, H 3.06, N 9.72.

2: Upon a solution of tdapb (50 mg, 0.0614 mmol) in CH_2Cl_2 (6 mL) were successively layered benzene (4 mL), methanol (4 mL), and a sonicated solution of $Ag(NO_3)$ (31 mg, 0.184 mmol) in methanol (6 mL). The vial was covered in aluminum foil, and the solvents were allowed to diffuse slowly over several days to afford colorless crystals of **2** (70 mg, 84 %). Elemental analysis: calcd for $Ag_3C_{54}H_{39}N_{12}O_9\cdot 1.5\,CH_2Cl_2$: C 45.93, H 2.89, N 11.59; found: C 45.85, H 2.91, N 11.85.

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